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THE DEVELOPMENT OF NEW PROTECTING/LEAVING GROUPS AND APPLICATION TO THE SYNTHESIS OF CAGE NITRAMINES

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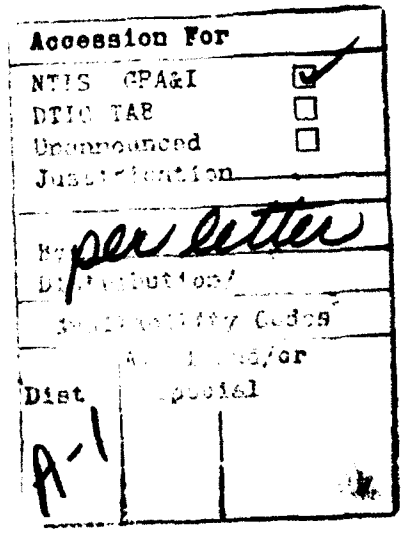

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INTRODUCTION

This final report details the results accomplished on Office of Naval Research (ONR) Contract No. N00014-88-C-0537 (SRI Project No. 6654). In the course of this study, we have accomplished the synthesis of a new, stable class of dinitramide salts that will have both fundamental scientific interest and practical applications. We have also developed a new type of condensation reaction for the synthesis of cage compounds and prepared new clathrates of CL-20 with significantly more energy than pure CL-20. The dinitramide salts are based on a newly discovered inorganic anion known as the dinitramide anion, $N(NO_2)_2^-$. The dinitramide anion is a uniquely stable, high oxygen density grouping that can be prepared in many different combinations, including the ammonium salts (SRI-12).

SIGNIFICANT RESULTS DURING CONTRACT

The results of these studies on the synthesis of energetic materials fall into three categories: (1) condensation reactions for ring and cage synthesis, (2) Clathrates of CL-20, and (3) synthesis of SRI-12.

CONDENSATION REACTIONS FOR RING AND CAGE SYNTHESIS

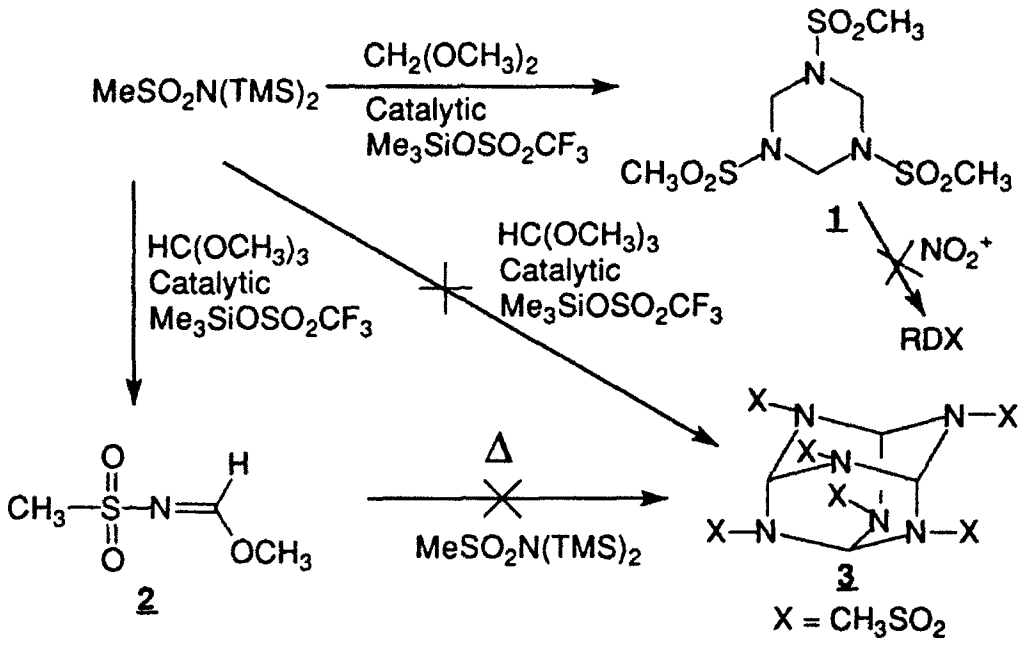
Sulfamate Protecting Groups

Development of improved methods for synthesizing of the CL-20 cage is of primary importance because of the need for new and simplified routes to CL-20. We investigated methodology based on using the phosphoramide or sulfamide moieties to build the scaffold required for the construction of cage molecules in this project. We previously observed that phosphoramide and sulfamide groups are effective as protecting groups in synthesis reactions and are good leaving groups in nitration reactions. Some progress has been made in this area through the synthesis of important preliminary compounds. Further research should lead to the synthesis of CL-20.

Our preliminary studies have shown phosphoramides to be excessively hydrolytically labile. To address this problem, we have investigated the reactions of anhydrous versions of glyoxal and formaldehyde with phosphoramides and sulfamides. From these preliminary results, we focused our attempts at cage synthesis on the reaction of mono- and bifunctional sulfonamides with formaldehyde and glyoxal. This strategy has not yet led to self-assembling molecules that provide us easy access to cage structures, but it still holds great promise. These studies have resulted in the synthesis of phosphoramide and sulfamide precursors to RDX, and we have undertaken the initial steps toward a CL-20 cage structure.

N,N-Bis-trimethylsilylmethanesulfonamide condensed cleanly with dimethoxymethane in the presence of Me_3Si-OTf catalyst to give the triazine **1** (see Scheme 1), which, surprisingly, could not be nitrated by nitronium tetrafluoroborate to give RDX.

N, N-Bis-trimethylsilylmethanesulfonamide was also condensed with trimethylorthoformate to give compound **2**, as shown in Scheme 1. Further attempts to



(1)

Scheme 1. Reaction of N,N-bis-trimethylsilylmethanesulfonamide with protected aldehydes and acids

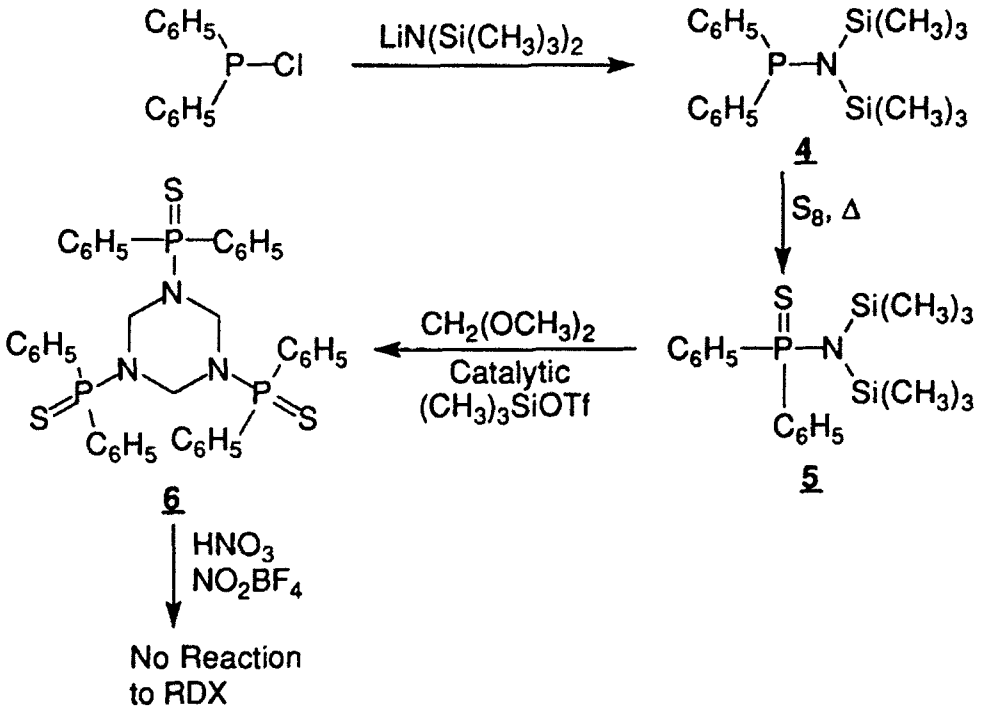
condense more N,N-bis-trimethylsilylmethanesulfonamide failed to give the desired product **3**. Direct reaction of N,N-bis-trimethylsilylmethanesulfonamide with trimethylorthoformate and catalytic quantities of Me_3Si-OTf also failed to give **3** directly. We believe that this reaction failed because the thermodynamic cost of rehybridizating the formyl carbon atom of **2** from sp^2 to sp^3 (as is the case in **3**) is prohibitive, because electrons have been donated from the esteric oxygen of **2** to the sulfonated nitrogen. The failure to rehybridize prevents the formation of **3** by oligomerization of **2** and N,N-bis-trimethylsilylmethanesulfonamide.

All attempts to convert compound **1** to RDX by reaction with NO_2BF_4 or in mixed sulfuric/nitric acids gave either unreacted starting material or, if the reaction was heated no product at all. Available evidence indicates that compound **1** is more stable to acid than RDX.

Thiodiphenylphosphate Protecting Groups

The second route that we attempted was to use thiodiphenylphosphoryl groups as the protecting/leaving groups for the synthesis of ring and cage compounds. The reaction sequence followed is shown in Scheme 2. In this reaction sequence, diphenyl chlorophosphine is reacted with lithium bis-N,N-trimethylsilylamide to give compound **4**. The phosphine derivative of compound **4** is converted to the thiophosphoramide by reaction with S_8 and heat to give compound **5**, which is then condensed cleanly with dimethylacetal and catalytic quantities of Me_3Si-OTf to give compound **6**. Two views of the crystal structure of compound **6** are shown in Figures 1 and 2.*

All attempts to convert compound **6** to RDX by nitration with nitric acid/nitronium tetrafluoroborate proved unsuccessful. We believe that this nitration reaction failed because of hydrolysis of the C-N bonds of the triazine occurring faster than nitration hence resulting in degradation of the ring system.



Scheme 2: Synthesis of Hexahydro-tris(N,N',N"-diphenylthiophosphate)-1,3,5-triazine

* All crystal structures in this project were determined by R. Gilardi, J. Flippen-Anderson, and C. George at the Laboratory for the Structure of Matter at the Naval Research Laboratory (NRL). The authors gratefully acknowledge their contributions.

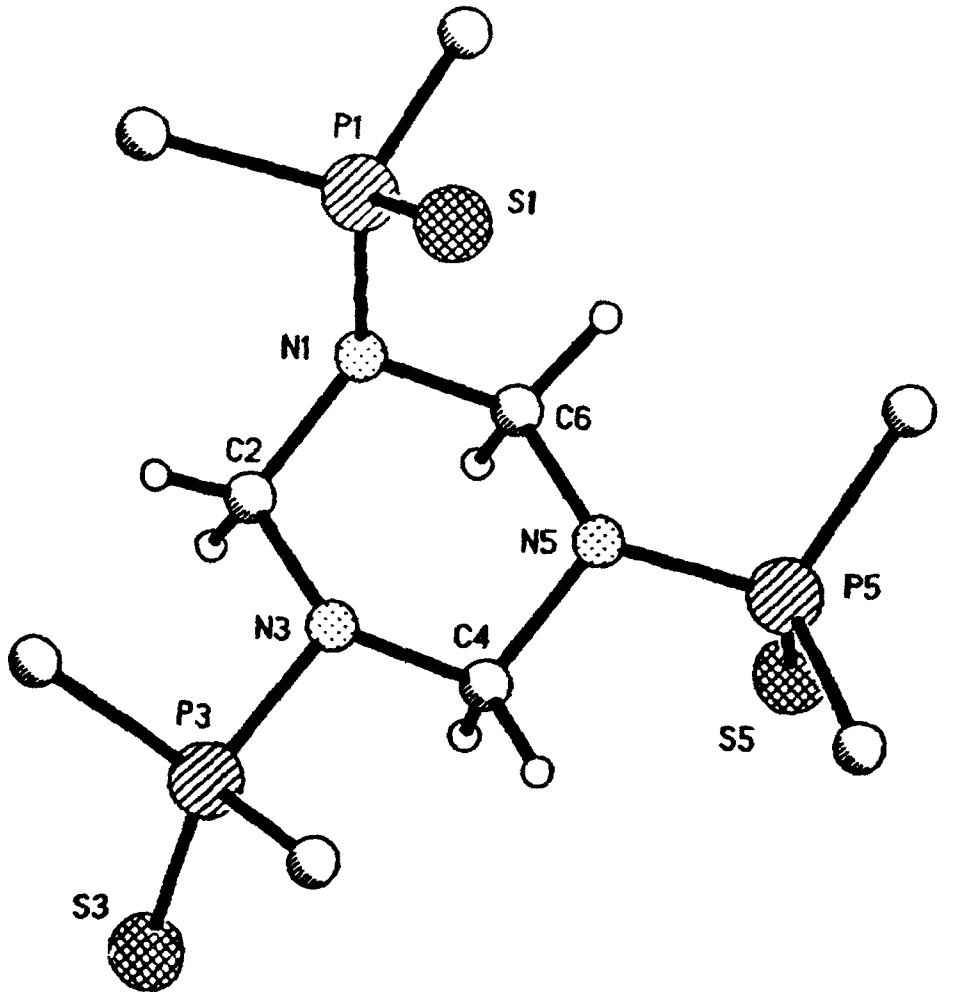


Figure 1. Partial crystal structure of hexahydro-tris(N,N',N"-diphenylthio(phosphate)-1,3,5-triazene (Compound **6**).

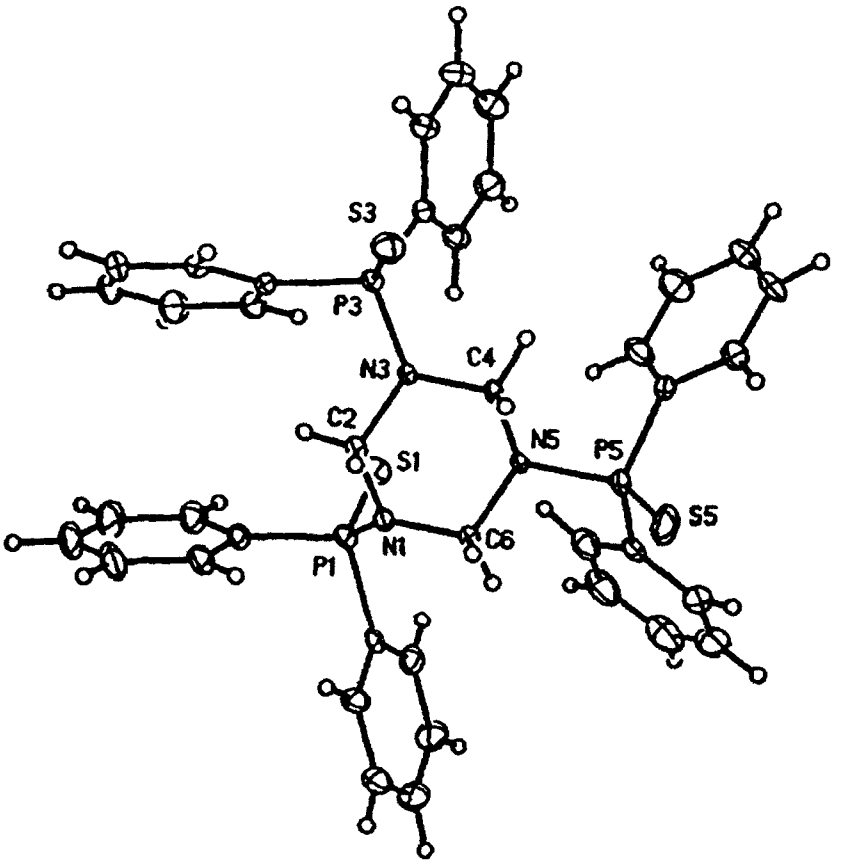
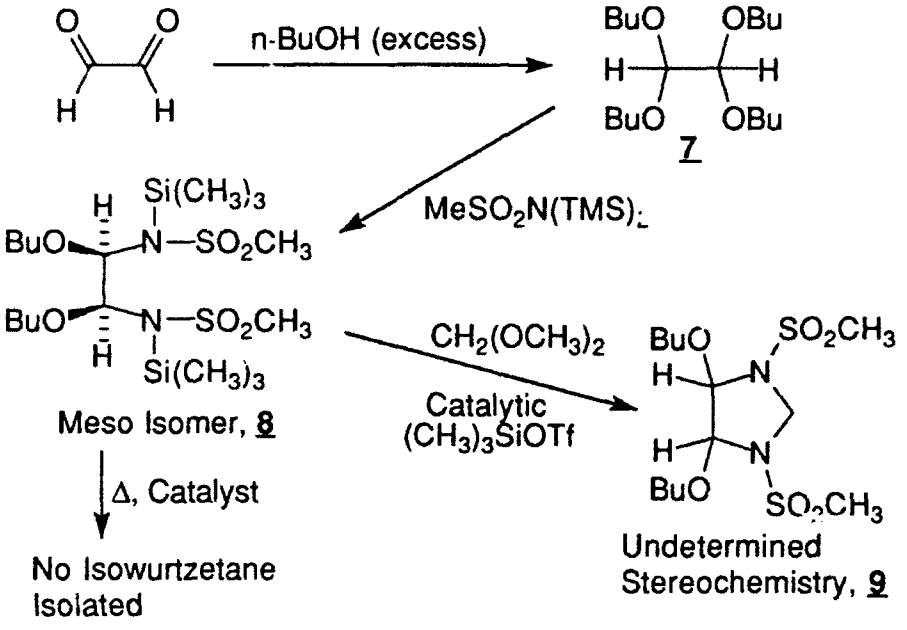


Figure 2. Crystal structure of hexahydro-tris(N,N',N"-diphenylthiophosphate)-1,3,5-triazene (Compound **6**).

Attempts to Synthesize Isowurtzitanes By Reaction With Sulfamides

We attempted to prepare isowurtzitanes by the reaction sequence shown in Scheme 3. First, glyoxal was converted to the tetra(n-butyl)diacetal (7) by reaction with n-butanol. Compound 7 was then condensed with N,N-bis(trimethylsilyl)methanesulfonamide to give compound 8 (crystal structure shown in Figure 3). To investigate the properties of compound 8, we reacted it with dimethylformal in the presence of catalytic Me_3Si-OTf to give compound 9, as shown in Scheme 3. Attempts to condense compound 8 with itself (twice) in the presence of a catalyst and heat failed to give the desired isowurtzitane or any identifiable products.



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Scheme 3. Attempted synthesis of isowurtzitanes by the condensation of glyoxal and N-methanesulfonate-N,N-bis(trimethylsilyl)amine.

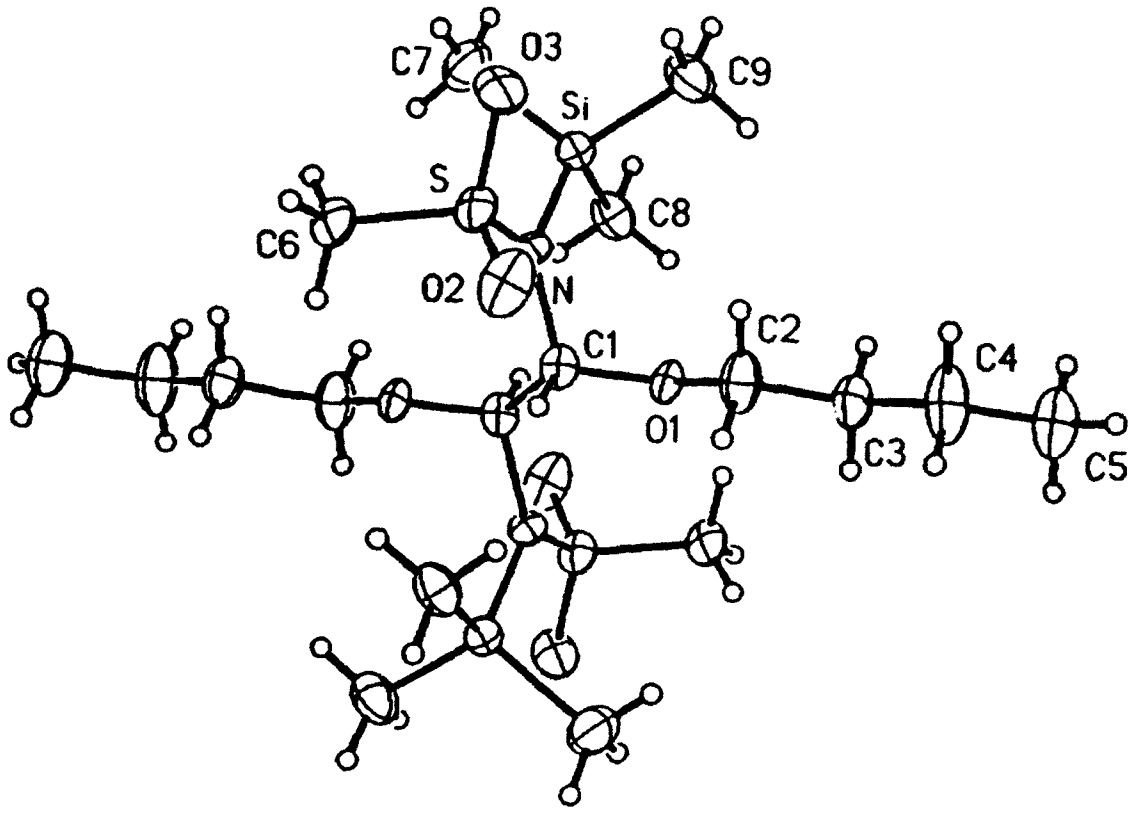


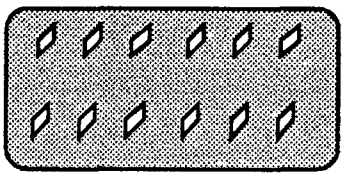
Figure 3. Crystal structure of *meso*-1,2-bis(N,N'-trimethylsilyl-N,N'-methyl-sulfonate)-1,2-bis(N'-butoxyl)ethane.

We believe that the condensation of compound **8** with itself failed to give the desired isowurtzitane cage structure because the polymerization reaction is kinetically favored. Additionally, there is a second possible pathway that goes through the elimination of butanol to give an unstable olefin.

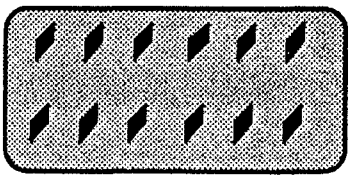
In summary, while we believe that this chemistry remains highly promising, further studies of the nitration chemistry of these systems are required to develop methods for direct removal of the phosphoramide and sulfamide protecting groups. Additionally, new conditions and substrates need to be developed to allow the direct synthesis of cage compounds using this methodology. Attempts at synthesis of the wurtzitane or isowurtzitane skeleton have not, thus far, yielded positive results. A wider variety of catalysts and conditions needs to be tried to determine the limitations of these reactions.

CLATHRATES OF CL-20

A promising way to improve new materials is to combine or modify their properties by using them as the hosts in the preparation of clathrates, crystals with completely enclosed cavities in which guest molecules are imprisoned. The synthesis of clathrate compounds from existing energetic compounds is a straightforward method for improving these existing materials by filling voids; it does not require a "start-from-scratch" synthesis of new energetic compounds. We illustrate graphically below how this approach would work within a molecular crystal.



Less energy dense crystal with unfilled cavities



Higher energy dense crystal having filled cavities

This combining of energetic materials holds promise because it may result in materials with improved properties such as increased energy or oxidizer density plus reduced sensitivity to friction, heat, or shock. We have demonstrated this concept by the synthesis of energetic clathrate derivatives.

The following terms are defined here to minimize confusion.

Clathrate: A crystal with completely enclosed cavities, so that guest molecules are imprisoned within the cavities.

Channel Complex: A crystal having long tunnels, layers, or channels that extend from the interior through to the surface of the crystal.

Host: A molecule that forms a crystal lattice with spaces large enough for the guest.

Guest: A molecule incorporated into the crystal structure of the host.

Inclusion Compound: Any crystal composed of a guest and a host.

We envision the possibility of one of the components of the clathrate acting as a molecular level shock absorber. The guest can absorb some of the energy of a shock through hydrogen bonds just as the hydrogen bonding operates in TATB to dramatically reduce its shock sensitivity. Thus, hydrogen bonding within the materials acts as a form of molecular insulation, minimizing repulsions or frictional forces between energetic molecules.

A second possible use of a clathrate is to fill the interstitial voids or cavities (which are present in all crystalline solids) with a fuel, a burn rate modifier, or more oxidizer. The voids lower the density and reduce the energy density of the ingredient. In essence, we seek to use the oxidizer as a host for a guest molecule incorporated into the crystal structure to create a clathrate or an inclusion complex.[1,2] Thus, our secondary goal is to synthesize energetic clathrates that increase the energy content of existing propellant ingredients.

In summary, the synthesis of clathrates from CL-20 may result in the following benefits:

- Creation of new classes of energetic materials having modified properties.
- Higher energy density, achieved by filling empty interstitial cavities of crystals with either oxidizers or fuels.
- Molecular level doping for burn rate modifiers
- Molecular level shock absorbers, resulting in decreases in sensitivity.
- Clathrates based on existing energetic materials.

- Molecular level stabilizer incorporation to increase shelf life of energetic materials by suppression of degradative reactions

We have prepared the first energetic clathrate of the CL-20 system. Initially, we attempted to prepare clathrates or inclusion complexes of CL-20 having ammonia as the guest, but these experiments were unsuccessful. We believe that these guests failed because the ammonia reacted with CL-20 to decompose the CL-20 molecule, presumably through a proton abstraction reaction, since ammonia is highly basic. This reaction had not been observed previously and is new chemistry for CL-20. To prevent this decomposition, we will need to explore other clathrates or inclusion complexes of CL-20, using nonbasic guests or guests having their base strength moderated with respect to ammonia.

The first clathrate prepared in this program, SRI-14, has a stoichiometry of 2 CL-20 to 1 HN_3. The resulting crystal has higher density, (2.015 g/cm^3) than CL-20 crystallizes faster than CL-20 alone in the same environment and is of higher quality. From our initial tests, this clathrate appears to have the same or better shock sensitivity. The x-ray crystal structure (Figure 4) shows the HN_3 sealed in a crystal having a stoichiometry of 2 CL-20 to 1 HN_3 (SRI-4). Figure 4 shows only two of the CL-20 molecules that compose the clathrate. A better perspective is shown in Figure 5, where four space-filling CL-20 structures are shown surrounding the central HN_3. The HN_3 is sealed into the crystal lattice by two more CL-20's (not shown) that are placed over the top and bottom of the HN_3 guest. The HN_3 cannot be removed from the crystal even under high vacuum, and thus we have a true clathrate composed of CL-20 and HN_3.

The second clathrate synthesized is composed of 2 CL-20 to 1 H_2O_2 (SRI-5). The crystal structure of this compound is shown schematically in Figure 6. The dotted lines in this crystal structure show the approximate best approaches for H-bonding. The thermogravimetric analysis (TGA) of SRI-5 is shown in Figure 7. This TGA is especially revealing, because the onset of weight loss shows a loss of 3.86 % of the weight of the sample, approximately equal to the weight of the H_2O_2 contained in the clathrate (3.88%).

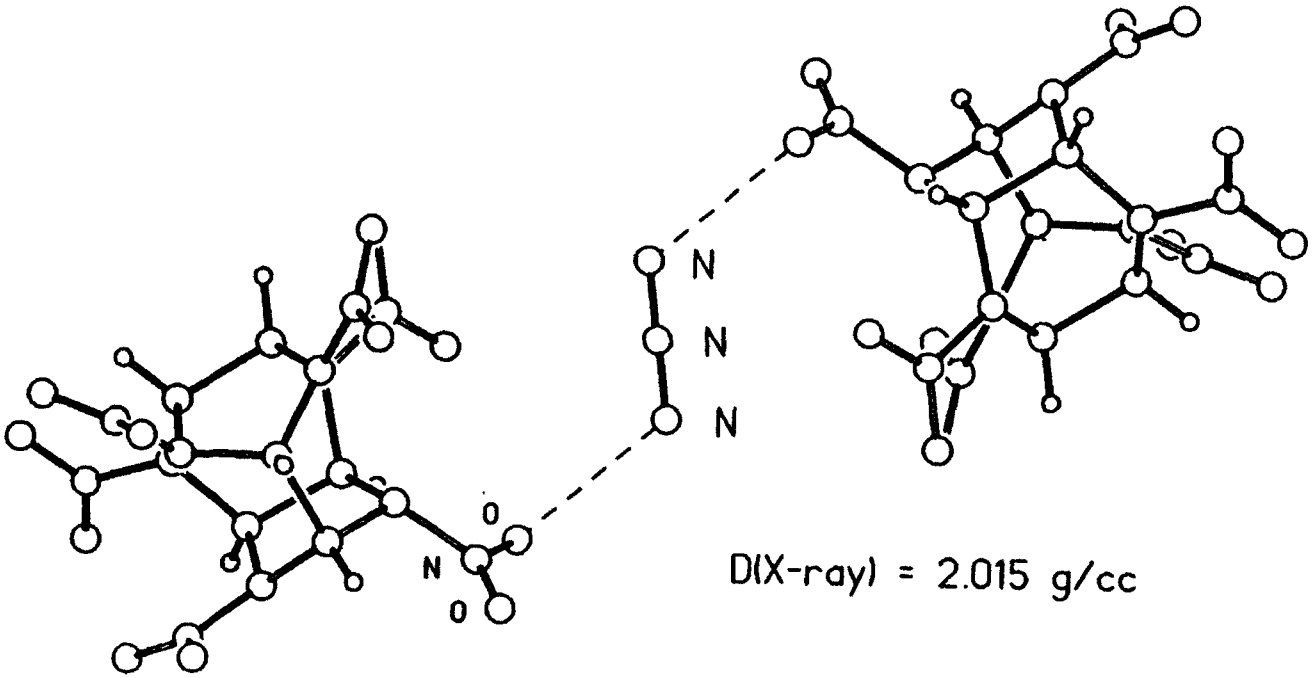


Figure 4. Crystal structure of SRI-4.

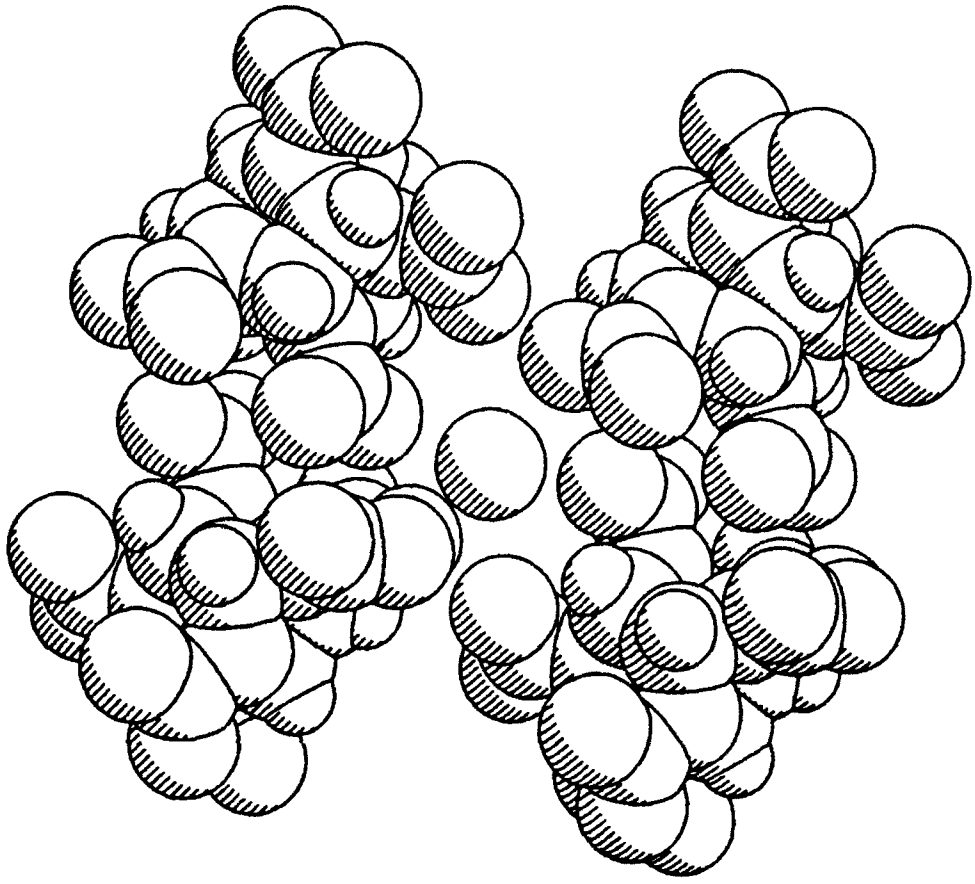


Figure 5. Crystal structure of SRI-4.

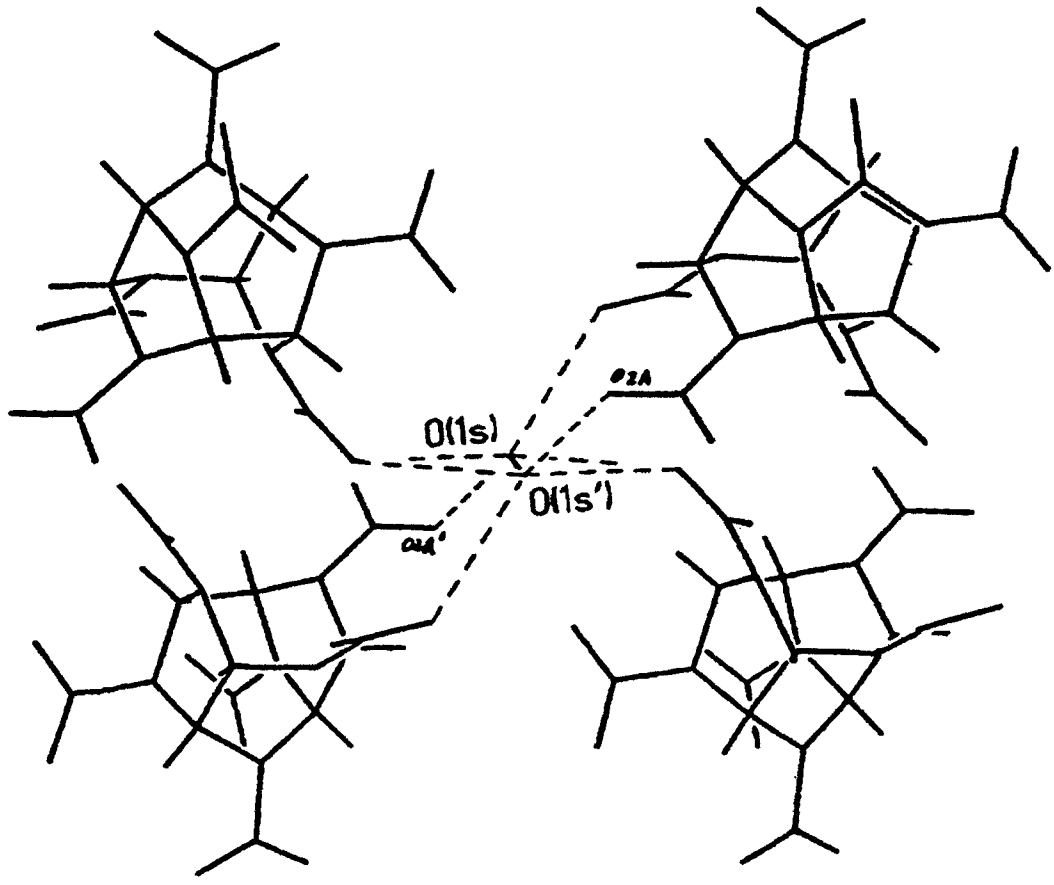


Figure 6. Crystal structure of SRI-5 showing oxygen closest approaches to CI-20.

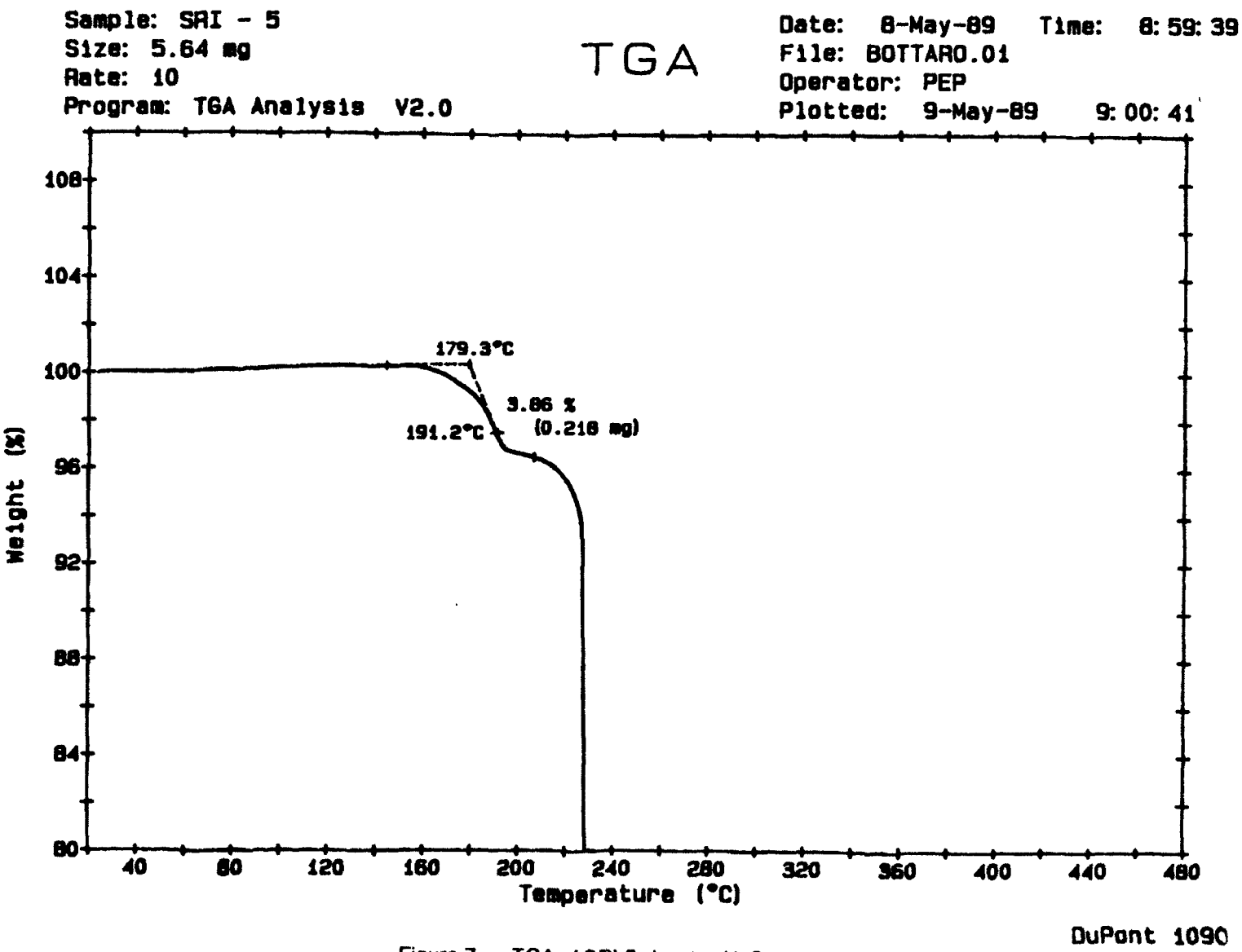


Figure 7. TGA of SRI-5 showing H_2O_2 loss.

More recently, we prepared a hydroxylamine clathrate of CL-20 (SRI-20). The crystal structure of this compound is shown in Figure 8. This compound was prepared following the suggestion† that inclusion of hydroxylamine in the CL-20 crystal would act to desensitize CL-20 to impact while also giving a higher density and ΔH_f than those of CL-20. SRI-20 was tested for drop weight sensitivity by Lawrence Livermore National Laboratory (LLNL): when compared with pure CL-20, no change in sensitivity was noted.

In Figure 8, SRI-20 is shown with the potential N- and O-centers of the hydroxylamine labeled as N,O and O, N, respectively, and with an additional hydrogen present. This presentation results frome ambiguities in the crystal structure determination because of scrambling in the orientation of the hydroxylamine in the cavity of the CL-20 crystal. The crystal structure shown in Figure 8 has dotted lines between the hydrogens on the hydroxylamine and the oxygens of the CL-20 to show the approximate H-bonding in the crystal lattice.

The differential scanning calorimetrigram (DSC) of the decomposition of SRI-20 is shown in Figure 9. An initial decomposition is shown at approximately 165°C, where presumably the hydroxylamine decomposes. This is followed by a much stronger decomposition of the CL-20 initiating at around 220°C. Further studies are required to determine whether the hydroxyamine is affecting the decomposition of the CL-20.

Our initial syntheses of clathrates are summarized in the Experimental section, below, and a copy of a paper we presented at a recent JANNAF meeting is attached as Appendix A. The compounds prepared are listed in Table 1.

† By R. Miller, Office of Naval Research.

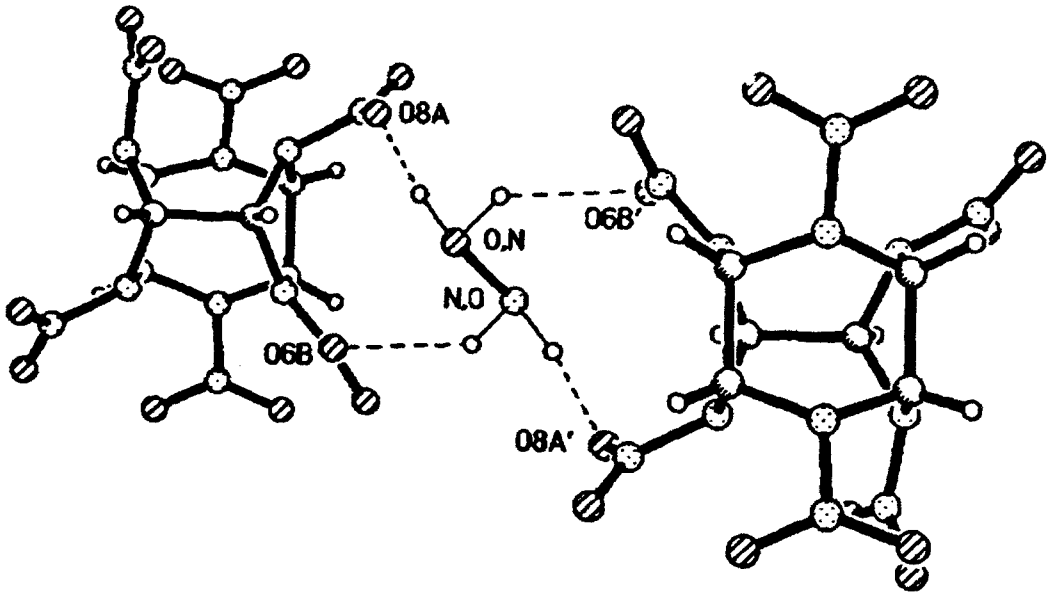


Figure 8. Crystal structure of SRI-8 showing N and O positions for hydroxylamine.

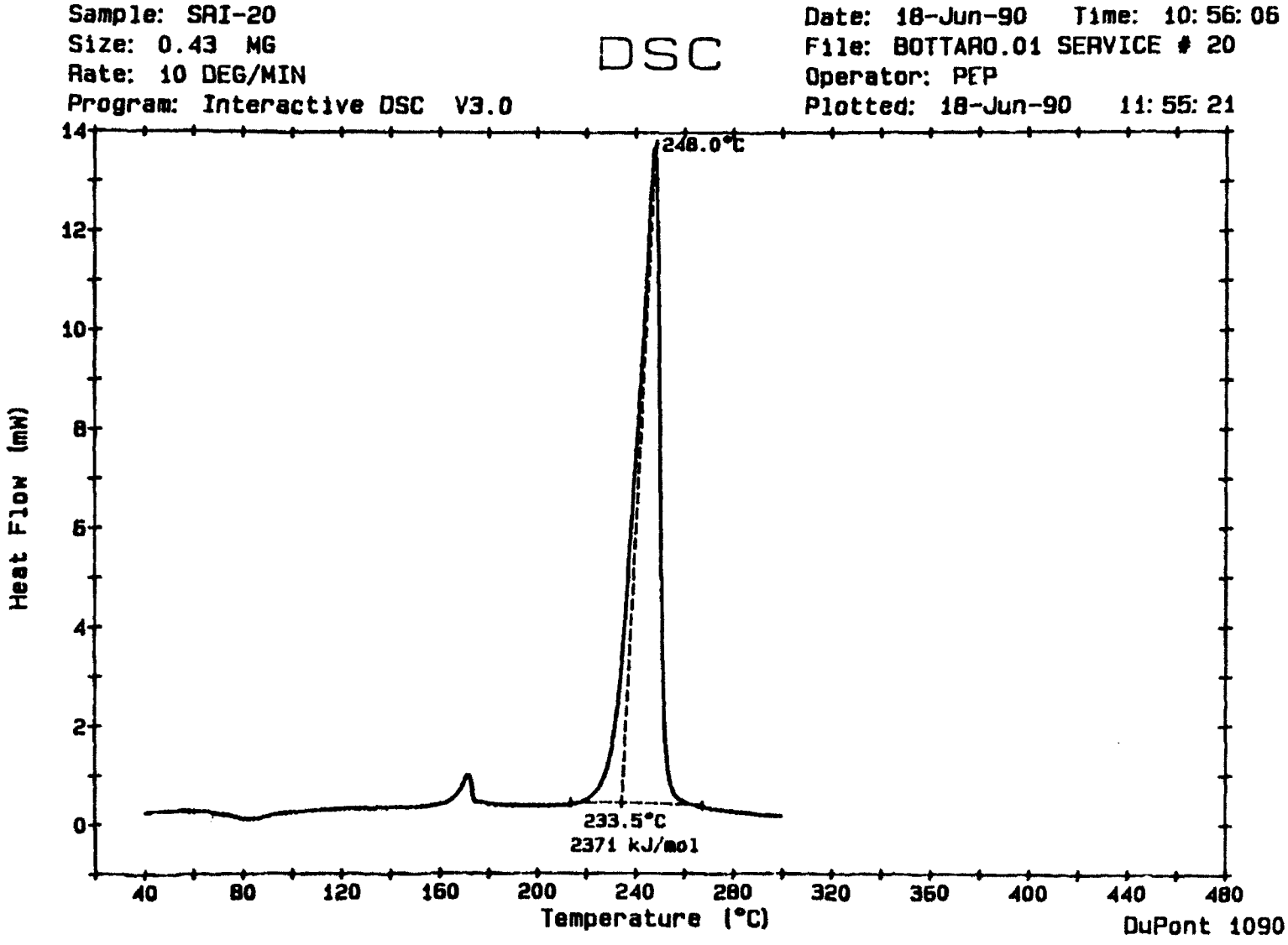


Figure 9. DSC of SRI-20.

Table 1

CL-20 CLATHRATE COMPOUNDS

Guest	Result
NH_3	Decomposes
HN_3	Crystal obtained (SRI-4) Stoichiometry of 2 CL-20 to 1 HN_3
H_2O_2	Crystal obtained (SRI-5) Stoichiometry of 2 CL-20 to 1 H_2O_2
NH_2OH	Crystal obtained (SRI-20) Stoichiometry of 2 CL-20 to 1 H_2O_2

DINITRAMIDE SALTS

We recently synthesized a completely new, stable class of inorganic oxidizers that will have both fundamental scientific interest and practical application to rocket propulsion (this work was done in cooperation with our SDI/ONR project, Contract no. N00014-88-C-0537). These oxidizers are based on a newly discovered inorganic anion known as the dinitramide anion, which has the formula $N(NO_2)_2^-$. The dinitramide anion is a uniquely stable, high oxygen density grouping that can be prepared in many different combinations, including the ammonium salt (SRI-12), the compound expected to be of most interest for rocket propulsion. Since the dinitramide anion has never been observed before, there is fundamental interest in its properties and structure, and much work needs to be performed to improve its synthesis and better understand its full impact. We have prepared many different dinitramide salts, including the lithium, cesium, ammonium, hydrazinium, hydroxylammonium, and guanidinium as well as other derivatives. The compounds prepared are summarized in Table 2.

Table 2

PROPERTIES OF DINITRAMIDE SALTS

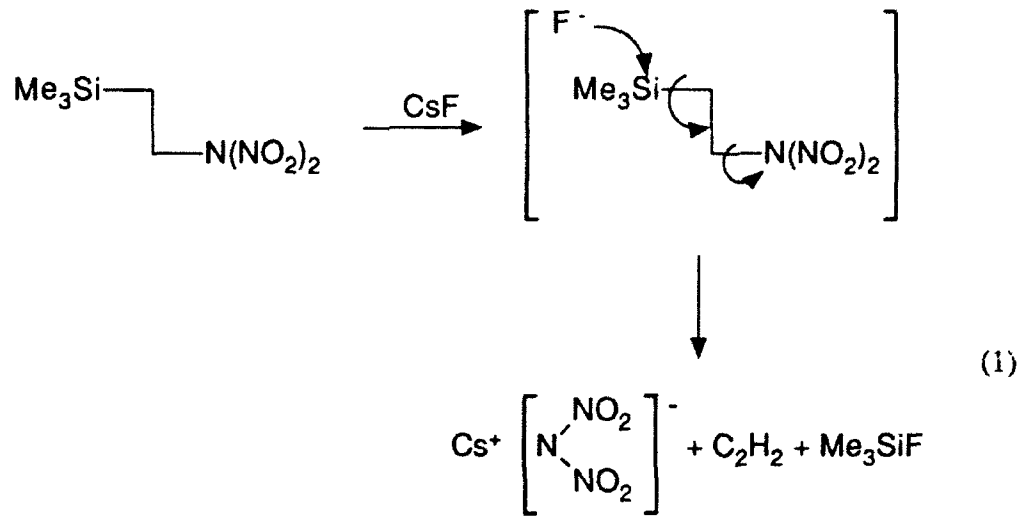
Name	Formula	Density[a] (g/cm^3)	ΔH_f[b] (kcal/mol)	
	$LiN(NO_2)_2$			
SRI-11	$CsN(NO_2)_2$	3.05 (x-ray)		
SRI-12	$NH_4N(NO_2)_2$	1.80 (x-ray)	-35.8[b]	(Measured)
SRI-13	$N_2H_5N(NO_2)_2$	1.83 (x-ray)	-8	(Estimated)
SRI-14	$(NH_2OH)_2HN(NO_2)_2$			
SRI-17	Cubane-1,4-$(NH_3N(NO_2)_2)$	1.77 (x-ray)		
SRI-19	Cubane-1,2,4,7-$(NH_3N(NO_2)_2)$	1.85 (x-ray)		
SRI-21	$C(NH_2)_3N(NO_2)_2$	1.67 (x-ray)	-40.7± 1.5[b]	
	(Measured)			
	$NH_3OHN(NO_2)_2$		-32	(Estimated)
For Comparison				
	$LiClO_4$	2.42	-91	
KP	$KClO_4$	2.53	-102.8	
	$CsClO_4$	3.33	-103.9	
AP	NH_4ClO_4	1.95	-70.7	
HAP	NH_3OHClO_4	~2	-66.5	

[a]Crystal structures determined by R. Gilardi, J. Flippin-Anderson, and C. George, Structure of Matter Laboratory, NRL.

[b]Heat of formation for SRI-12 determined at NWC, China Lake; that for SRI-21 determined at Los Alamos National Laboratory.

Cesium Dinitramide

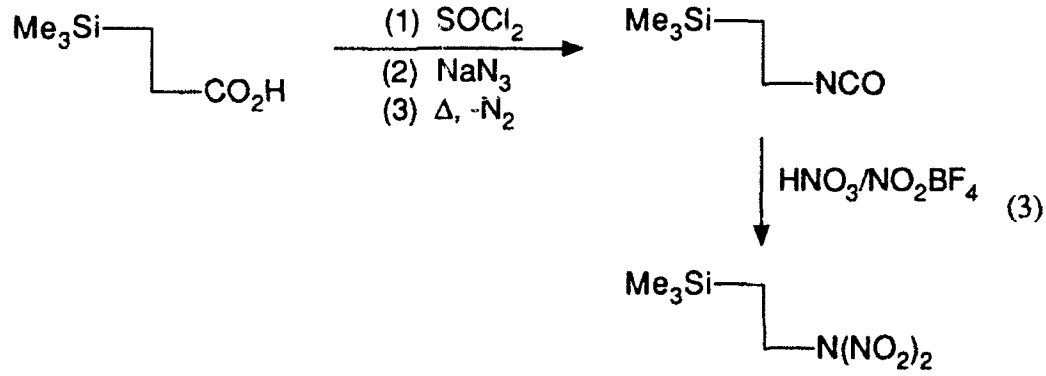
Cesium dinitramide is synthesized by a β-elimination reaction with cesium fluoride ion and 1-(N,N-dinitramino)-2-trimethylsilylethane to give a fluoride-ion-catalyzed elimination of trimethylsilylfluoride, ethylene, and the desired cesium dinitramide (SRI-11). Scheme 4 shows the reaction.



(1)

Scheme 4. Synthesis of cesium dinitramide.

1-(N,N-Dinitramino)-2-trimethylsilylethane is synthesized by a recently discovered reaction between an isocyanate and a mixture of nitric acid and nitronium tetrafluoroborate (Scheme 5).[3] The publication describing this synthesis[5] is attached as Appendix C.



(3)

Scheme 5. Synthesis of 1-(N,N-dinitramino)-2-trimethylsilylethane.

The x-ray crystal structure of cesium dinitramide (determined by Gilardi and co-workers at NRL) is shown in Figure 10. The crystal structure presents two cesium

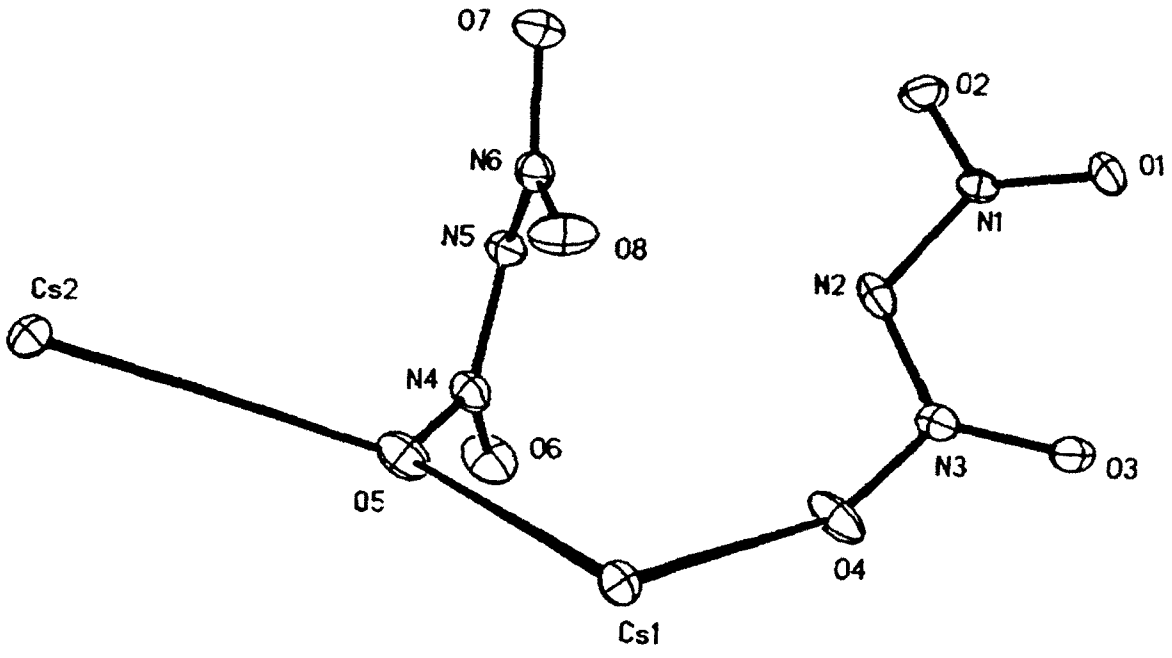
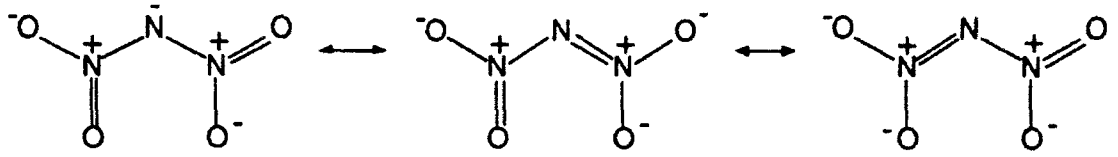


Figure 10. Crystal structure of $CsN(NO_2)_2$ (SRI-11).

dinitramide molecules, with the ionic interaction between cesium and the oxygen of the dinitramide shown by dashed lines. Note that the closest approach of the cesium ion to the dinitramide ion is through the oxygens of the nitro groups and not through the central nitrogen of the dinitramide. This packing behavior of the cation is seen in all dinitramide crystal structures, which implies that the highest charge density is found on the nitro oxygens in the crystal lattice rather than the central amide group.



Cesium dinitramide has a melting point of 87°C followed by the onset of exothermic decomposition at 175°C (DSC, Figure 11). Its density is 3.05 g/cm^3. The dinitramide ion is stable to base. Cesium dinitramide has a UV maximum at 284 nm [ε (H_2O) = 4.24 x 10^3 l mol^{-1} cm^{-1}]. Further studies of the thermal and solution properties of this anion are under way.

Other counterions can be substituted for cesium either by using alternative fluoride ion sources or by passing the cesium dinitramide through an ion-exchange column (Eq. 1). Several other salts that have been prepared using these methods as shown in Table 2.

$$CsN(NO_2)_2 \xrightarrow[\text{Ion Exchange}]{M^+} M^+ N(NO_2)_2^- \qquad (1)$$

The crystal structures of dinitramides show N-N bond distances between those of a single bond and a double bond, indicating resonance stabilization of the charge and a significantly stronger N-N bond than is found in conventional nitramines or dinitramines. Some of the resonance forms of the dinitramide ion are shown below, with the negative charge localized on the central nitrogen or delocalized out on either of the two nitro groups. In crystalline packings, it appears that the negative charge is predominantly on the oxygen.

The bond angles and distances in dinitramide salts are summarized in the two structures below, and typical bond distances and angles are given in Table 3. These structures give the average bond distances and angles for nine different dinitramide salts.

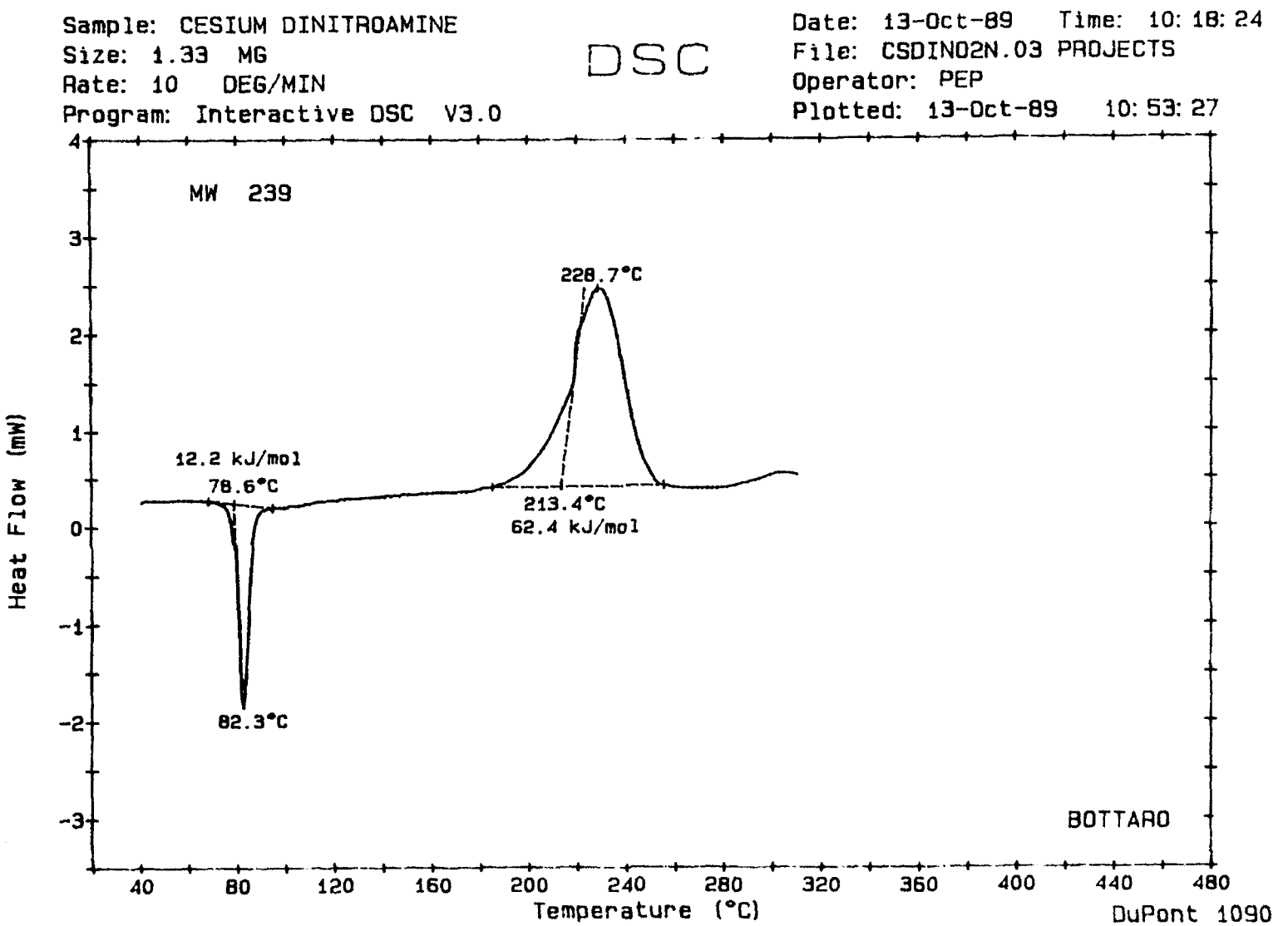


Figure 11. DSC of $CsN(NO_2)_2$ (SRI-11).

As can be seen from these averages, the N-N bond distance is almost exactly halfway between a single and a double N-N bonding distance. The N-O bond distances for the nitro groups are close to those observed in other nitro compounds. The N-N-N bond angle is less than that for sp^2 hybridization and greater than that observed for sp^3 hybridization.

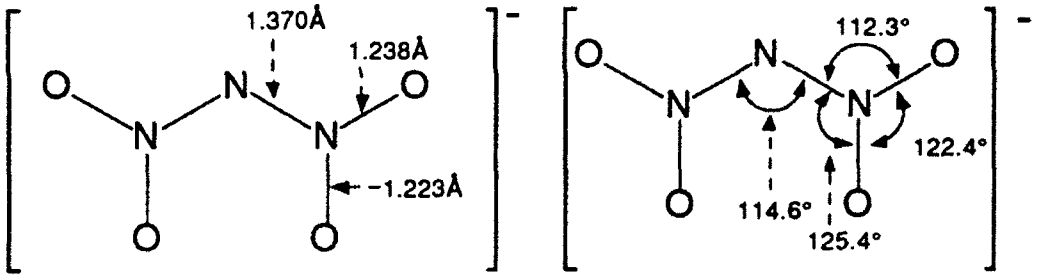


Table 3.

TYPICAL BOND DISTANCES FOR NITROGEN CONTAINING COMPOUNDS

Bond	Typical Length
N-N	1.451 Å (substituted hydrazine
N=N	1.25 Å
N=O	1.22 Å (nitro)
O-N-O bond angle	124° (aromatic)

Ammonium Dinitramide (ADN, SRI-12)

The most interesting dinitramide salt for practical applications is the ammonium derivative (SRI-12). Samples of ammonium SRI-12 have been provided to the Naval Weapons Center (NWC) at China Lake where itse heat of formation and sensitivity parameters have been measured. The group at NWC has burned a small sample of ADN in a test to simulate a rocket motor and have found that it burns completely, leaving with no residue. The NWC group confirms that samples using ammonium dinitramide as the oxidizer qualitatively burn as rapidly as CL-20 and faster than HMX. Quantities of SRI-12

have been synthesized and delivered to commercial companies for further testing and formulation.

The immediate application for SRI-12 is as a clean burning replacement for ammonium perchlorate (AP) in propellant formulation that also results in a gain in performance. AP leaves a heavy hydrochloric acid/smoke trail on burning. The chlorine in the smoke trail has been identified as a major contributor to ozone depletion in the stratosphere, and the smoke trail makes rockets more vulnerable to detection and tracking. The substitution of SRI-12 for AP would eliminate the HCl trail, since there is no chlorine in the oxidizer. Further, NASA has calculated that substitution of SRI-12 for AP in the space shuttle solid fuel boosters would give a 14% (8 seconds I_{sp}) improvement in performance, which translates into 4 tons more into orbit with each launch. SRI-12 has been burned in a small scale propellant test at NWC-China Lake. In this test it qualitatively had a burning rate twice that of a HMX based sample similarly prepared. All tests to date show that SRI-12 should have acceptable properties for solid fuel boosters.

The original synthesis of SRI-12, as was reported in our international patent applications,[5,6] is show in in Scheme 4 plus equation (1) where $M^+ = NH_4^+$. The patent application that resulted from work done on this ONR contract is attached as Appendix B.

We obtain approximately 25% overall yield from this route based on 3-trimethylsilylpropionic acid. We will not discuss in this document the current route for the synthesis of SRI-12, it will be reported in a document. It is a significant improvement over the route shown above.

The crystal structure for SRI-12 is shown in Figure 12. The crystal structure again shows that the closest approaches are between the cation and the oxygens of the dinitramide anion. This is illustrated much more clearly in Figures 13 and 14. In Figure 13, one ammonium cation is shown in the presence of the four closest dinitramide anions. The dotted lines illustrate the closest approaches (H-bonding) between the anion and cation. Figure 14 shows the opposite case, one dinitramide anion surrounded by the four nearest ammonium ions.

Figure 15 shows a view of the dinitramide ion down the plane of the molecule. The two nitro groups in all the dinitramide salts are out of plane with respect to each other, probably the result of non-bonded repulsion. This is an excellent demonstration of the

steric effects that the nitro groups have on each other. We predict that the dinitramide ion would be planar were there not a steric penalty imposed by the nitro groups.

SRI-12 has good thermal properties. Its DSC and TGA are shown as Figures 16 and 17, respectively. The DSC of SRI-12 shows the melting point onset at approximately 88°C and the onset of decomposition at 145°C. The TGA shows no weight loss until above 160°C, with complete weight loss by 240°C. The heat of formation of SRI-12 was measured at NWC, China Lake. The value obtained is -35.8 kcal/mol.

Hydrazinium Dinitramide (SRI-13)

The crystal structure of hydrazinium dinitramide and its DSC are shown in Figures 18 and 19, respectively. This compound was prepared to take advantage of the heat of formation that is obtained from the use of hydrazinium derivatives, which is higher than that of ammonium derivatives. Unfortunately, hydrazinium dinitramide is highly shock (impact) sensitive and thus has no practical value. Additionally, as observed in the DSC, the melting point is slightly lower than that of the ammonium derivative, further reducing the possibility of this compound having practical value.

Hydroxylammonium Dinitramide and Hydroxylammonium-Hydroxylamine Dinitramide (SRI-14)

We attempted to prepare the hydroxylammonium dinitramide salt because of the interest in obtaining a material having increased oxygen density. This compound would be comparable to hydroxylammonium perchlorate or nitrate. Unfortunately, studies in this laboratory have shown hydroxylammonium dinitramide to be a liquid.

However, we were able to isolate the hydroxylammonium-hydroxylamine dinitramide derivative as a crystalline solid. The x-ray crystal structure of this compound is shown in Figure 20. The crystal lattice contains both a hydroxylammonium and a hydroxylamine for each dinitramide anion present. We have been informed R. Gilardi at NRL that the crystal structure has another unusual feature: there is hydrogen bonding between both the oxygen and nitrogen of the hydroxylamine. This feature can be seen in Figure 20.

The DSC of hydroxylammonium-hydroxylamine dinitramide (not shown) indicates that the onset for melting of this derivative is near 75°C and the thermal onset for decomposition is around 150°C. The melting point is slightly lower than that of the

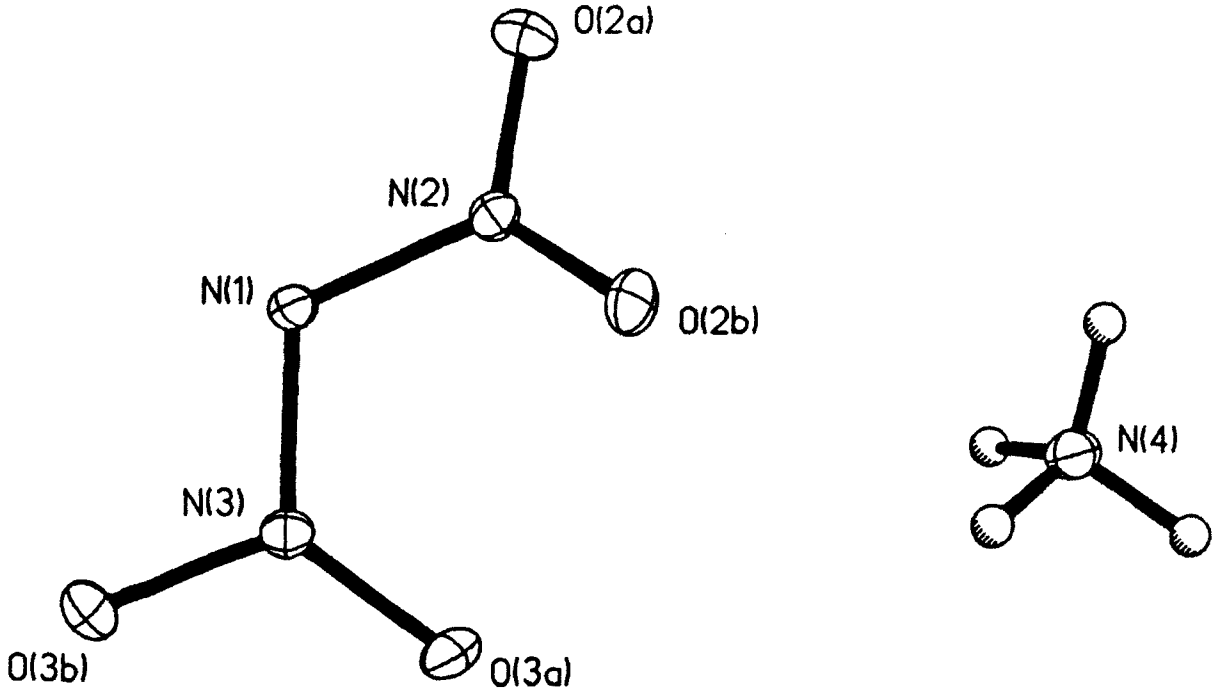
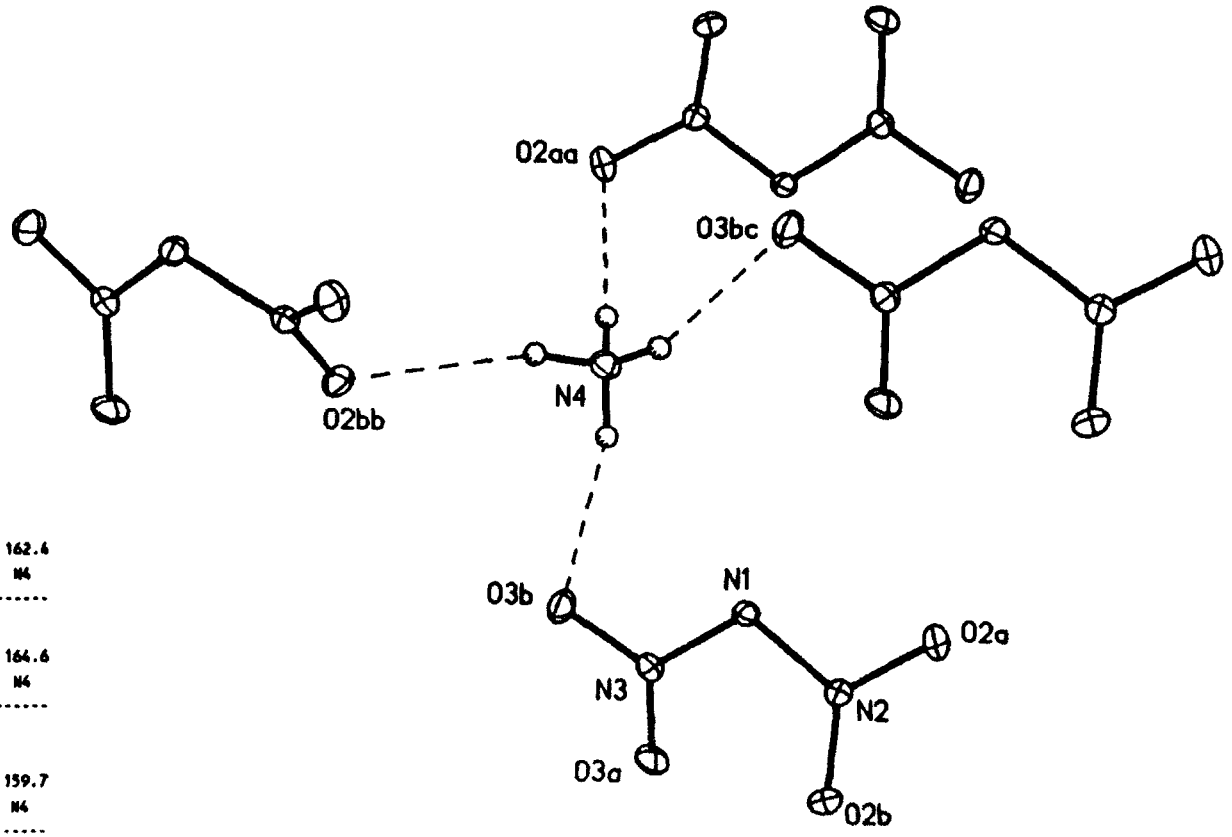


Figure 12. Crystal structure of ammonium dinitramide (SRI-12).



H1	N4	0.834	
H1	O2AA	2.143	162.6
			N4
H2	N4	0.852	
H2	O3B	2.172	164.6
			N4
H3	N4	0.834	
H3	O3BC	2.235	159.7
			N4
H4	N4	0.878	
H4	O2BB	2.282	164.3
			N4

Figure 13. Partial crystal lattice view showing closest approach of 4 dinitramide anions to the ammonium ion.

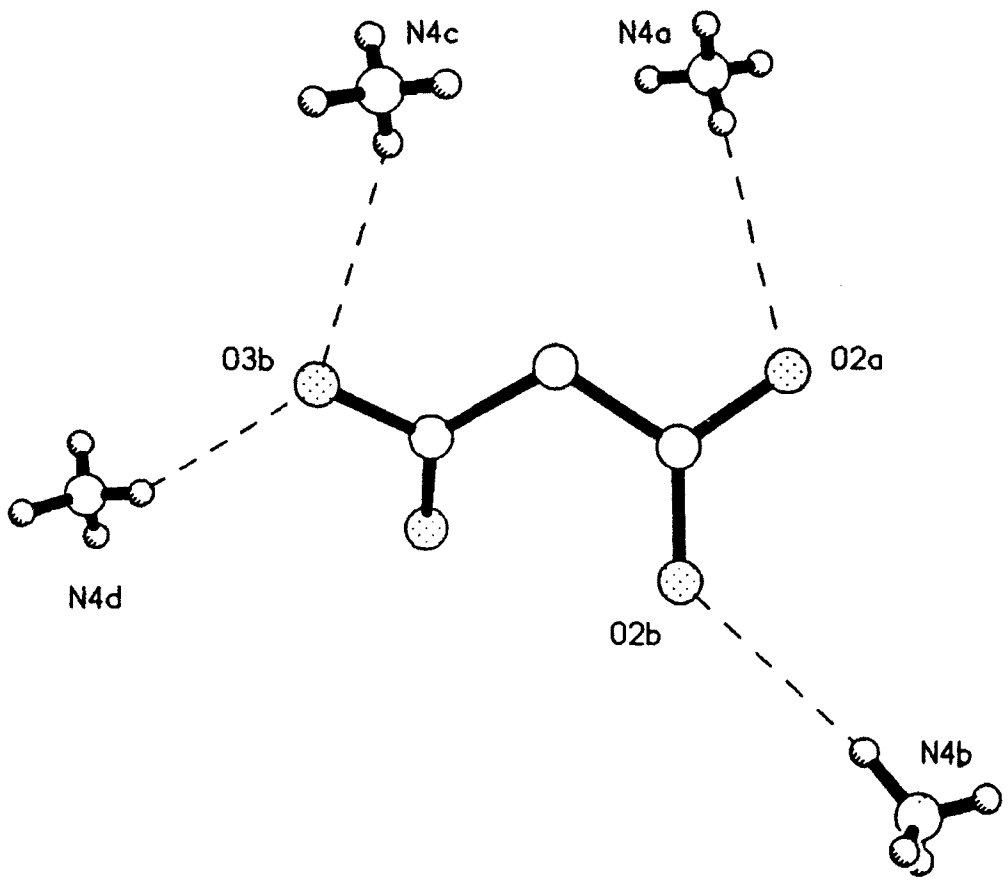


Figure 14. Partial crystal lattice view showing closest approach of 4-ammonium ions to one dinitramide anion.

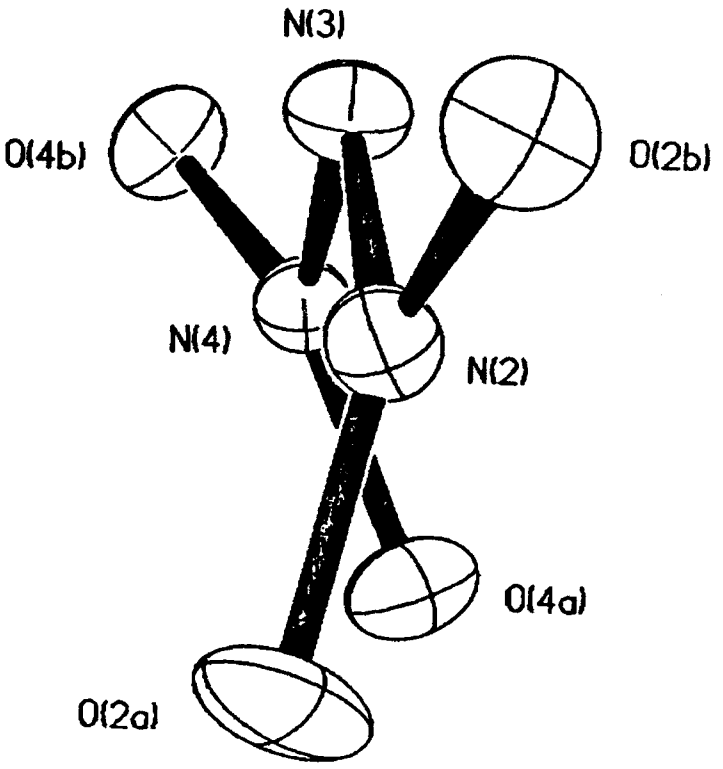


Figure 15. View of dinitramide ion down the plane of the ion.

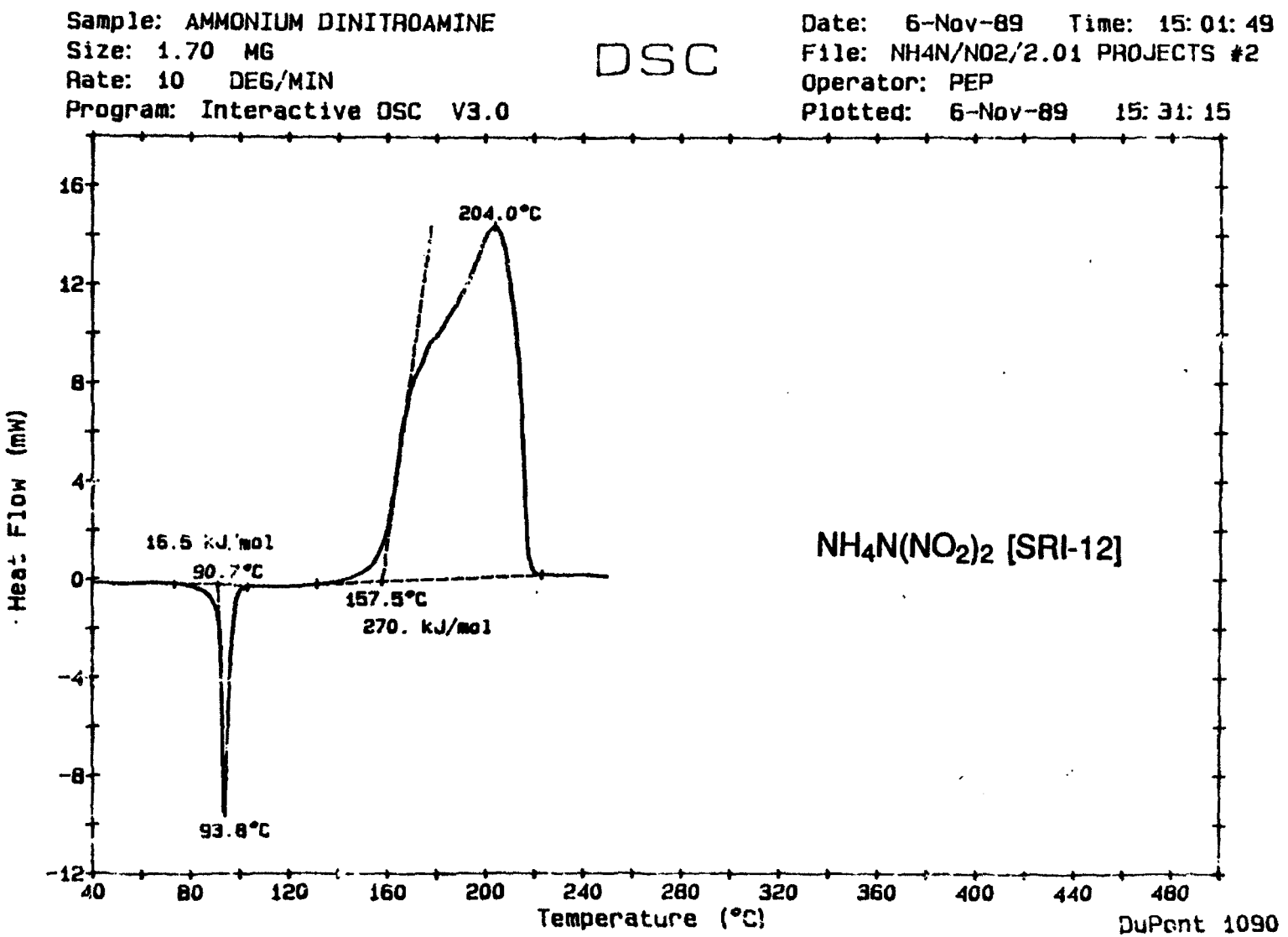


Figure 16. DSC of ammonium dinitramide.

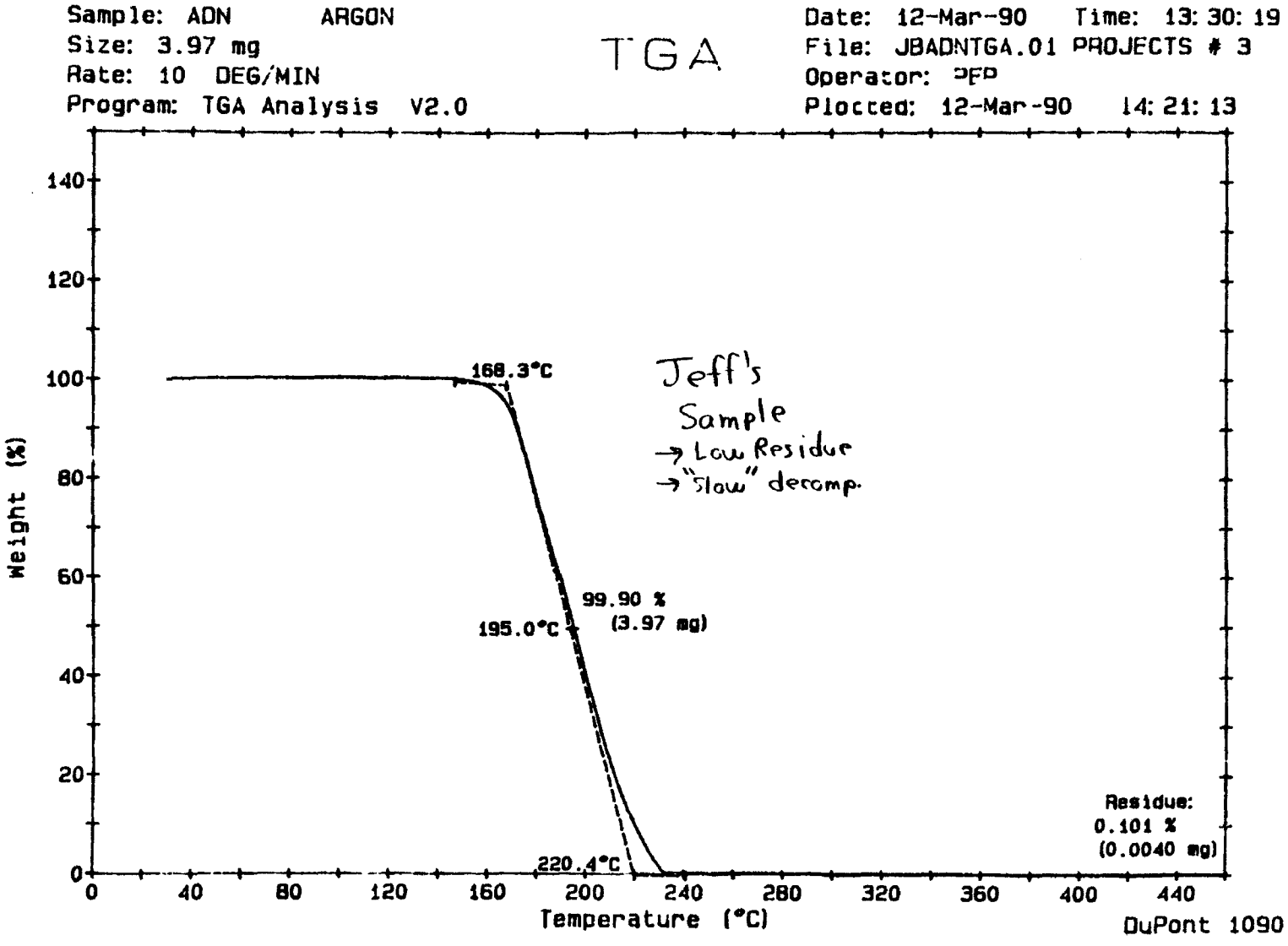


Figure 17. TGA of ammonium dinitramide.

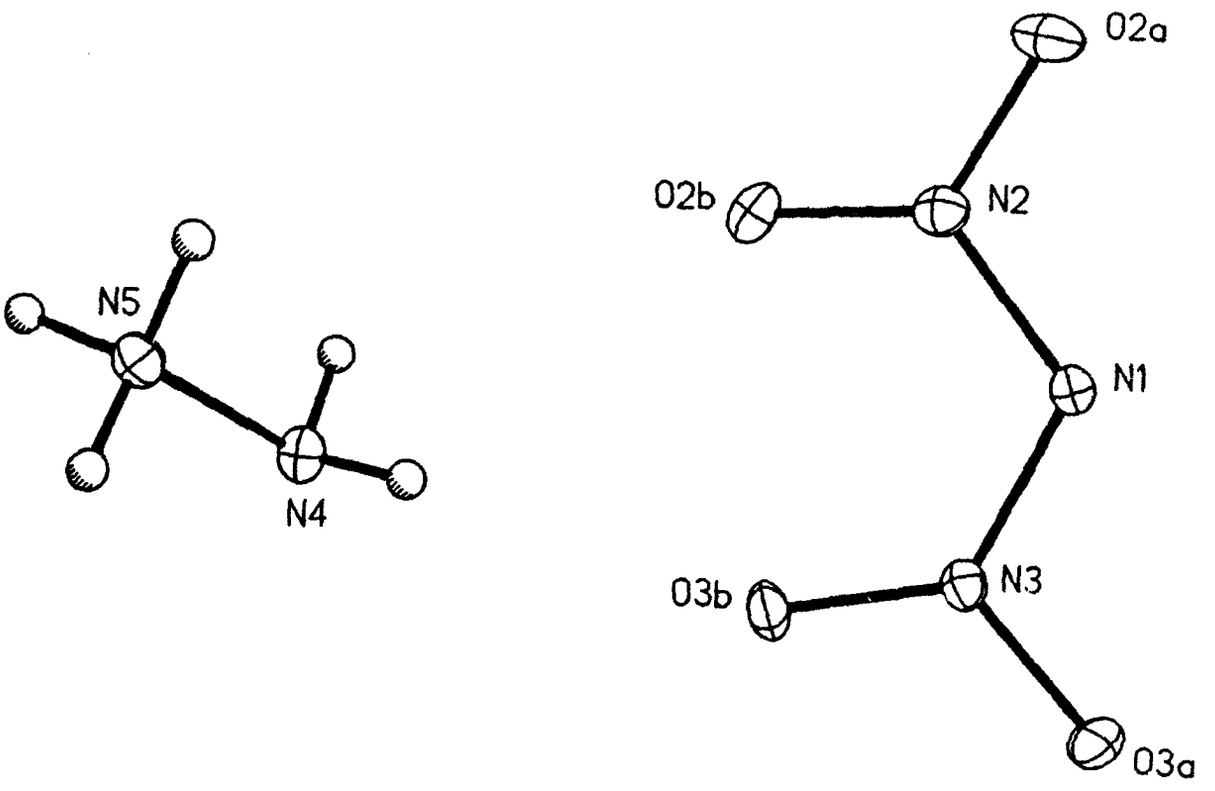


Figure 18. Crystal structure of hydrazinium dinitramide (SRI-13).

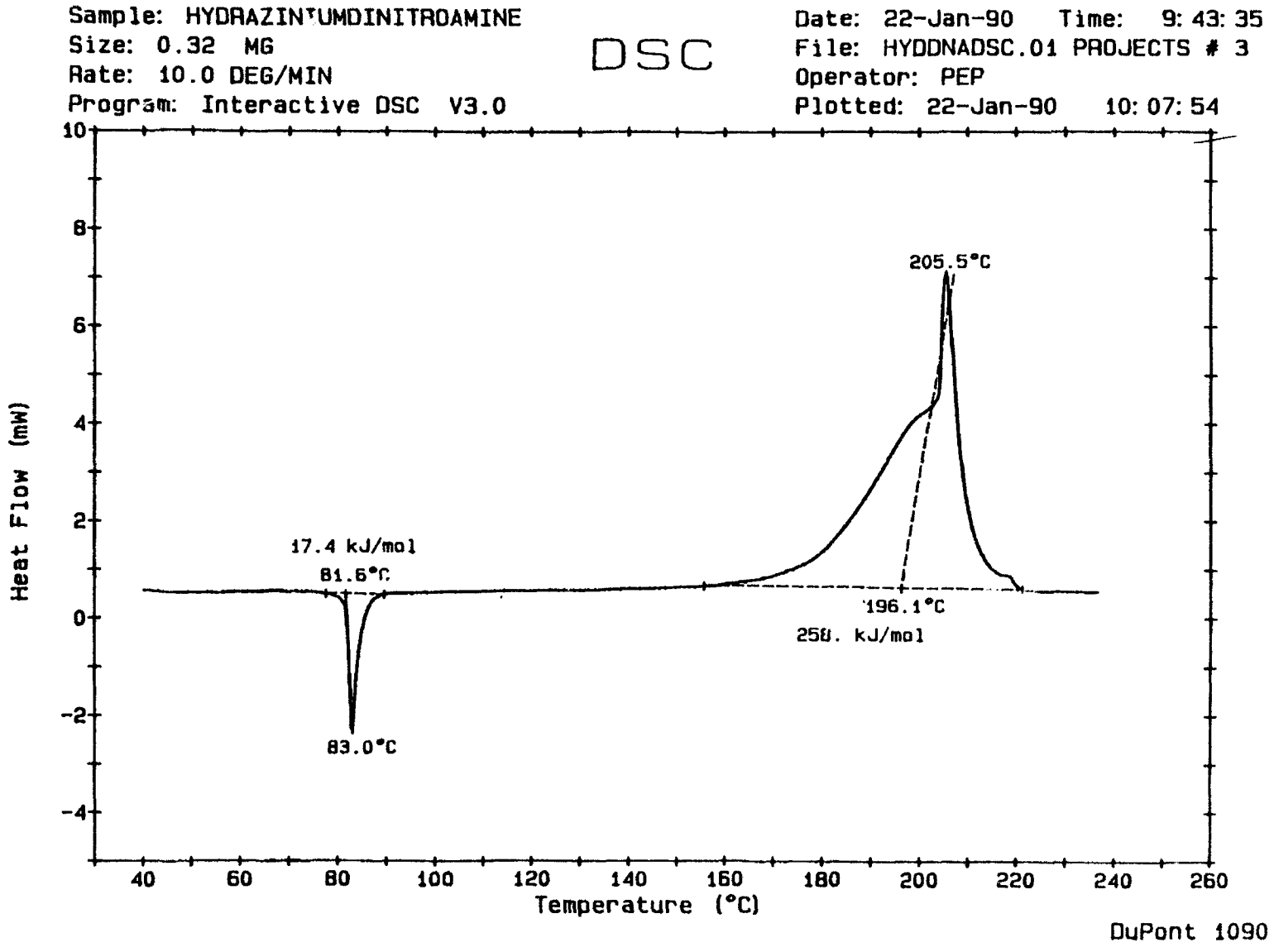


Figure 19. DSC of hydrazinium dinitramide (SRI-13).

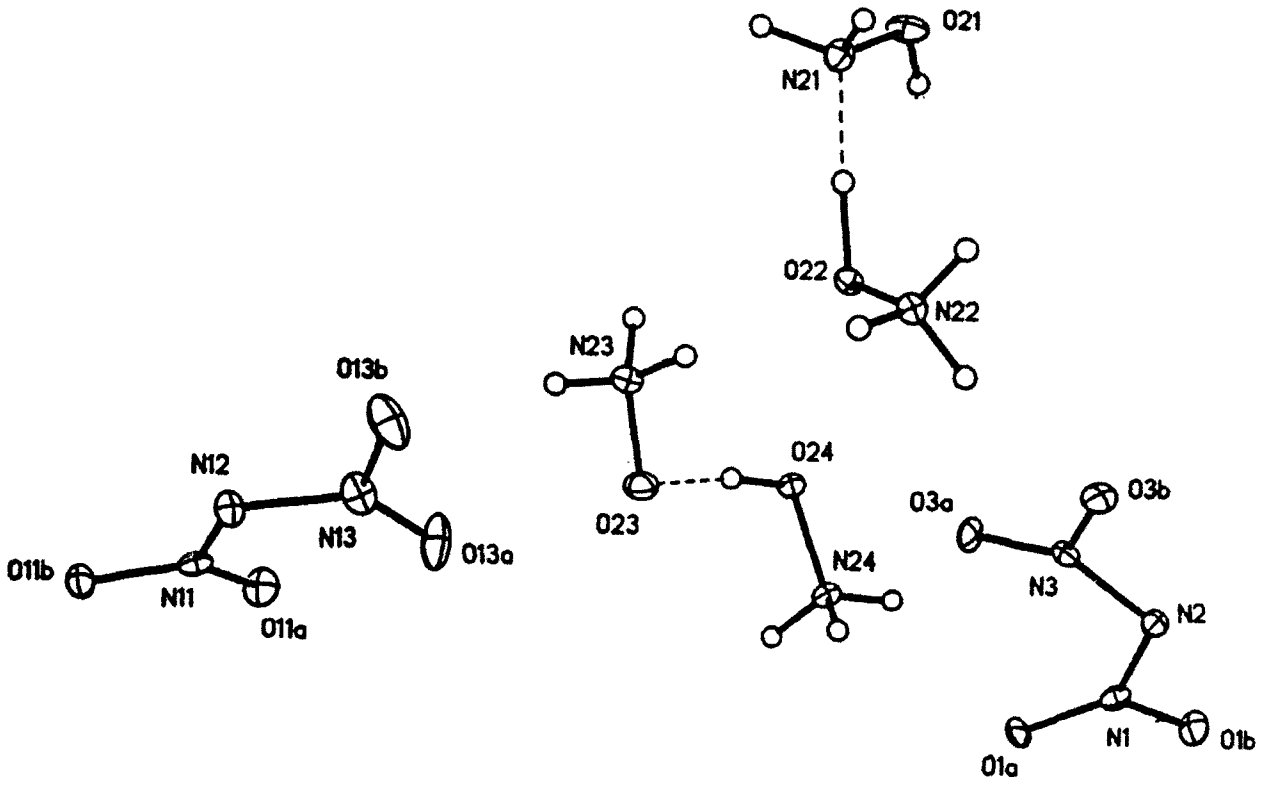


Figure 20. Crystal structure of SRI-14.

ammonium derivative, but the decomposition onset is near that of the ammonium salt. Qualitative determination of the impact (shock) sensitivity showed this compounds to be considerably more sensitive than the corresponding ammonium derivative. This derivative may find application as a liquid gun propellant.

Guanidinium Dinitramide (SRI-21)

Guanidinium dinitramide was prepared because we believed that it would have reduced shock and thermal sensitivity as compared to other dinitramide salts, but initial measurement of its impact sensitivity indicates that this is not the case. The impact sensitivity is approximately equal to that of the ammonium derivative. These tests along with a measurement of the heat of formation of the guanidinium derivative, were performed at Los Alamos National Laboratory (LANL) through the courtesy of Dr. Michael Coburn.

The heat of formation measured for this salt at LANL is -40.7 ± 1.5 kcal/mol. Thus, guanidinium dinitramide has a fairly high heat of formation as compared to the perchlorate (-74.1 kcal/mol) or nitrate derivatives (-93 kcal/mol).

The x-ray crystal structure of guanidinium dinitramide is shown in Figure 21. In this crystal structure, two guanidinium dinitramide salt molecules are shown, with the proposed hydrogen bonding between the anions and cations being indicated by dashed lines. A high degree of hydrogen bonding is inherent in this salt. Figure 22 presents a more comprehensive view of the crystal lattice, showing just how extensive the hydrogen bonding is. One item of note in Figure 22 is the large holes or gaps that are observed in the crystal lattice. The presence of these gaps may explain why the density of the guanidinium derivative is so unexpectedly low, only 1.67 g/cm^3. This low density is probably the factor that most limits the usefulness of guanidinium dinitramide as a potential energetic material.

The thermal properties of guanidinium dinitramide are interesting. The DSC shown in Figure 23 indicates what appears to be a phase change at around 110°C, with the melting point onset near 140°C. This melting point is surprisingly high for a dinitramide salt and is only matched or exceeded in the cubane derivatives (see below). Further investigations need to be done to determine if a true phase change occurs or whether it is due to the presence of trace impurities in the crystals. The onset for decomposition is again near

150°C, as is seen in most other dinitramide salts and appears to be characteristic of dinitramide derivatives in general.

Cubane-1,4-bis(ammonium dinitramide) (SRI-17)

Cubane-1,4-bis(ammonium dinitramide) was the first of two cubane compounds prepared under this program and our SDI/ONR project, Contract no. N00014-88-C-0537. TIts x-ray crystal structure is shown in Figure 24. One unique aspect of this crystal is the high degree of twist observed in the dinitramide anions, as can be seen in the crystal structure. This twist causes the two nitro groups in the dinitramide anions to be rotated out of plane with respect to each other to a high degree. Surprisingly, this twist in the dinitramide anions does not appear to create any special instability in the thermal properties of this compound. In the DSC (Figure 25), there is no melting point for this compound and the onset for decomposition is moved up to approximately 170°C. The combination of the absence of a melting point and this very high decomposition onset is unique among dinitramide salts.

Unfortunately, the observed density for this compound, 1.77 g/cm^3, is not high, nor is the compound particularly well oxidized. The presence of the cubane should give it a positive heat of formation (no heat of formation has been measured), but this is not enough to make it a desirable explosive derivative.

Cubane-1,2,4,7-tetrakis(ammonium dinitramide) (SRI-19)

Cubane-1,2,4,7-tetrakis(ammonium dinitramide) was the second of the two cubane compounds prepared under this program and our SDI/ONR project, Contract no. N00014-88-C-0537. The x-ray crystal structure is shown in Figure 26. The hydrogen bonding in this compound is of interest. The oxygens of one dinitramide anion interact with two ammonium ions on one face of the cubane. This hydrogen bonding pattern is repeated for all four dinitramide ions. A comprehensive view of the crystal lattice is shown in Figure 27. In this view of the crystal lattice, it is easy to see how each of the cubane-1,2,4,7-tetrakis(ammonium dinitramide)s interacts with its neighbor. Each successive cubane-1,2,4,7-tetrakis(ammonium dinitramide) appears to be just slightly offset to allow the dinitramide ions to slip between each other, thus allowing for good packing in the crystal lattice. The overall density of this compound is low, only 1.85 g/cm^3, and the compound is quite sensitive to shock, which limits its value. The overall heat of formation should be

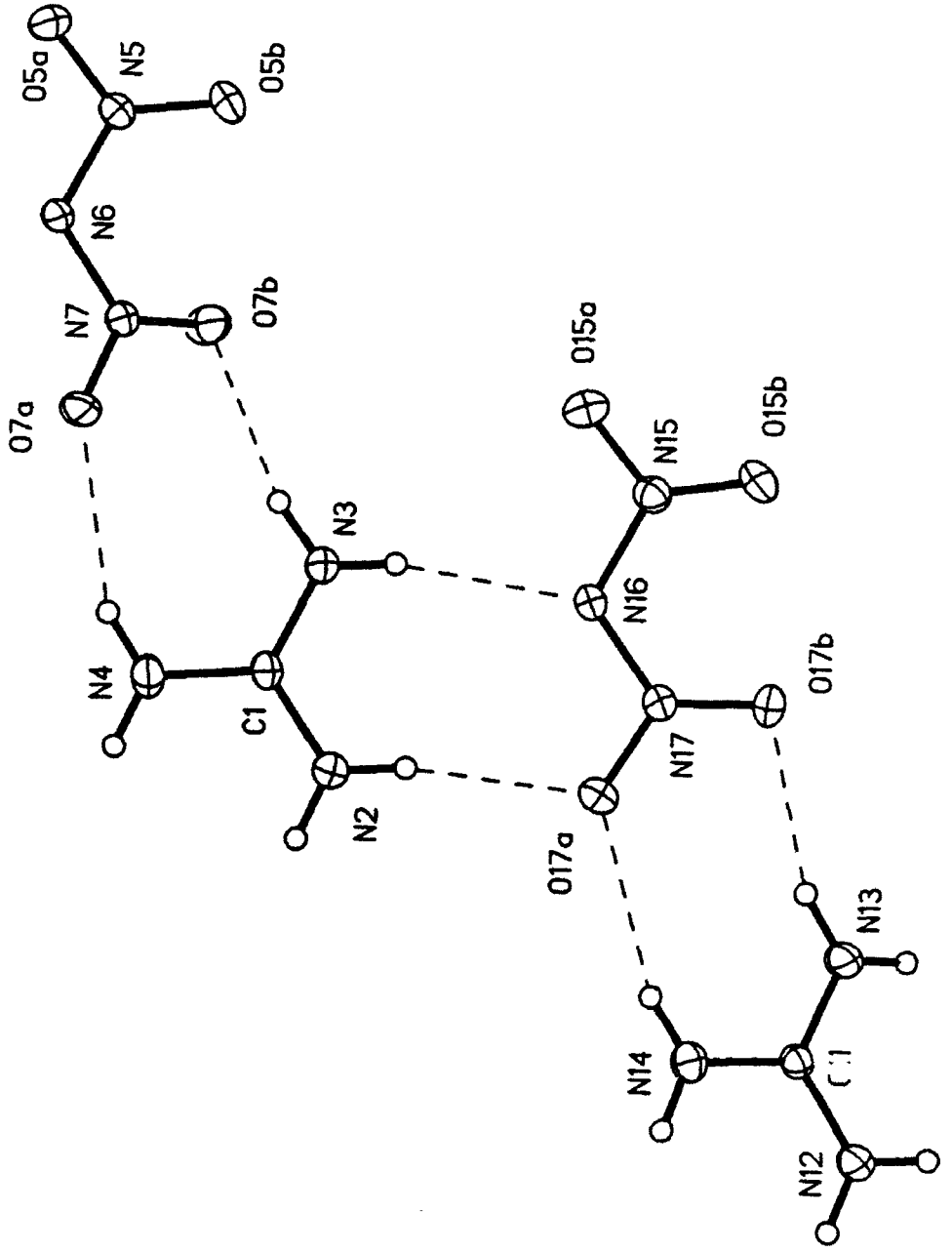


Figure 21. Crystal structure of guanidinium dinitramide (SRI-21) showing 2 molecules in view.

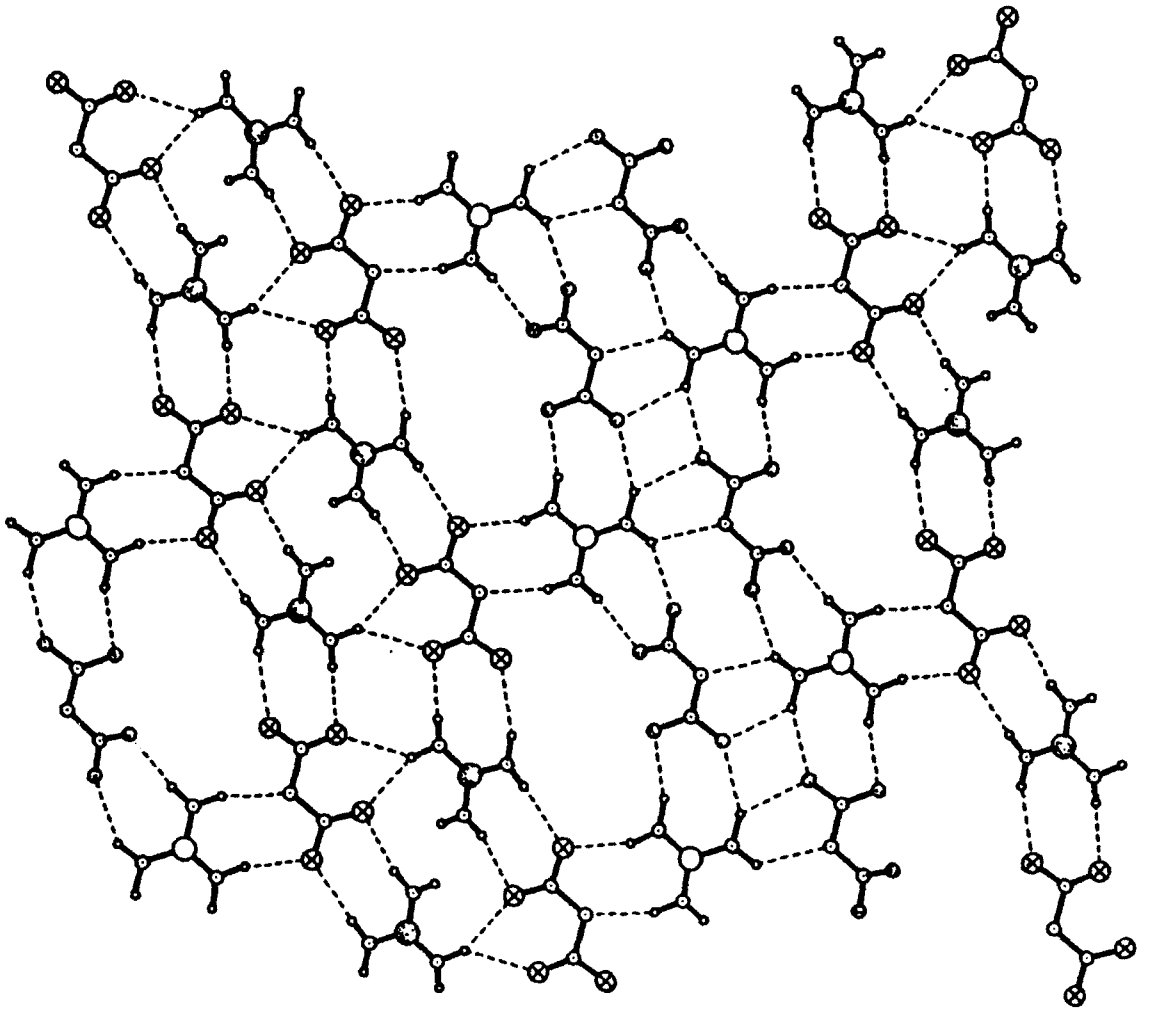


Figure 22. View of crystal lattice of guanidinium dinitramide.

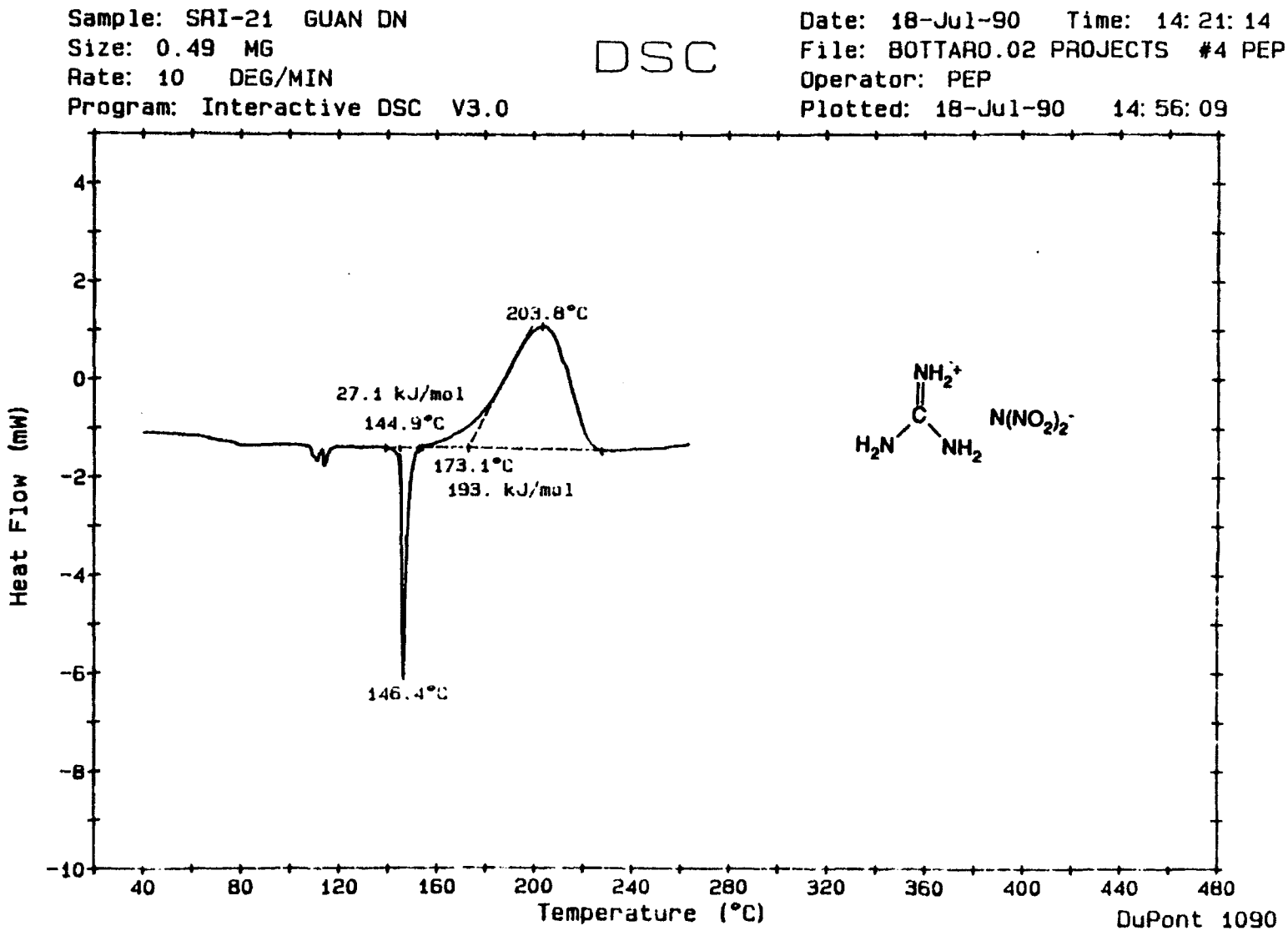


Figure 23. DSC of guanidinium dinitramide.

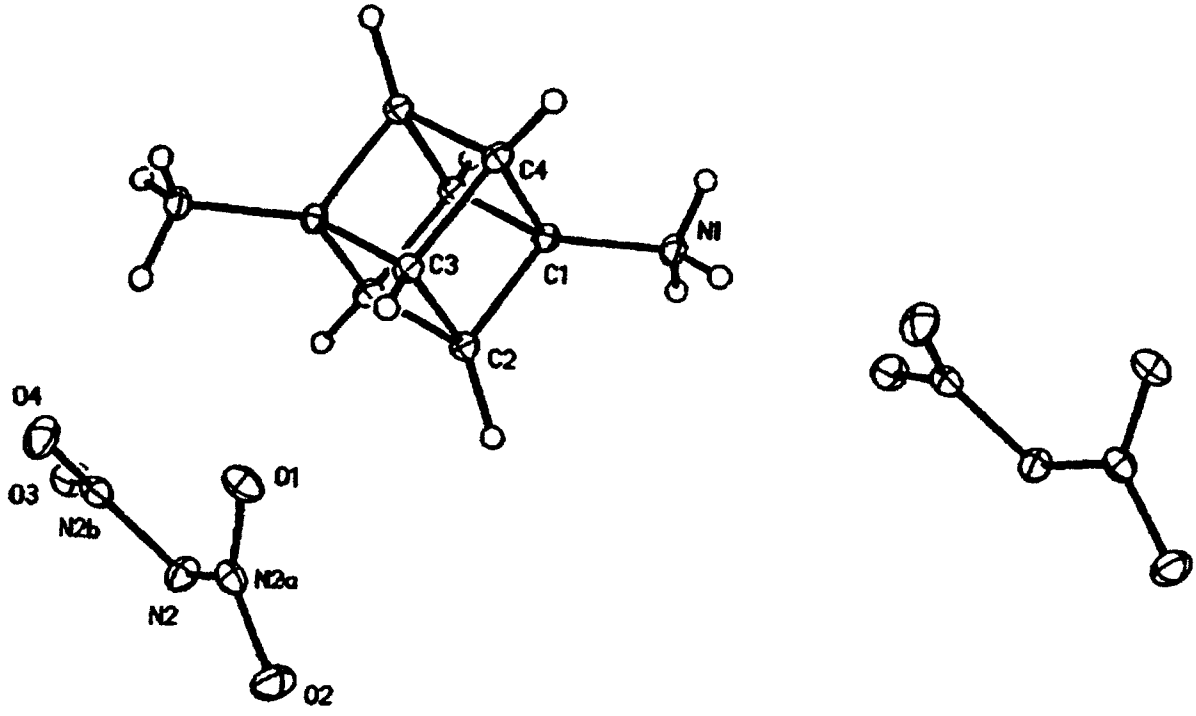


Figure 24. Crystal structure of cubane-1,4-bis(ammonium dinitramide).

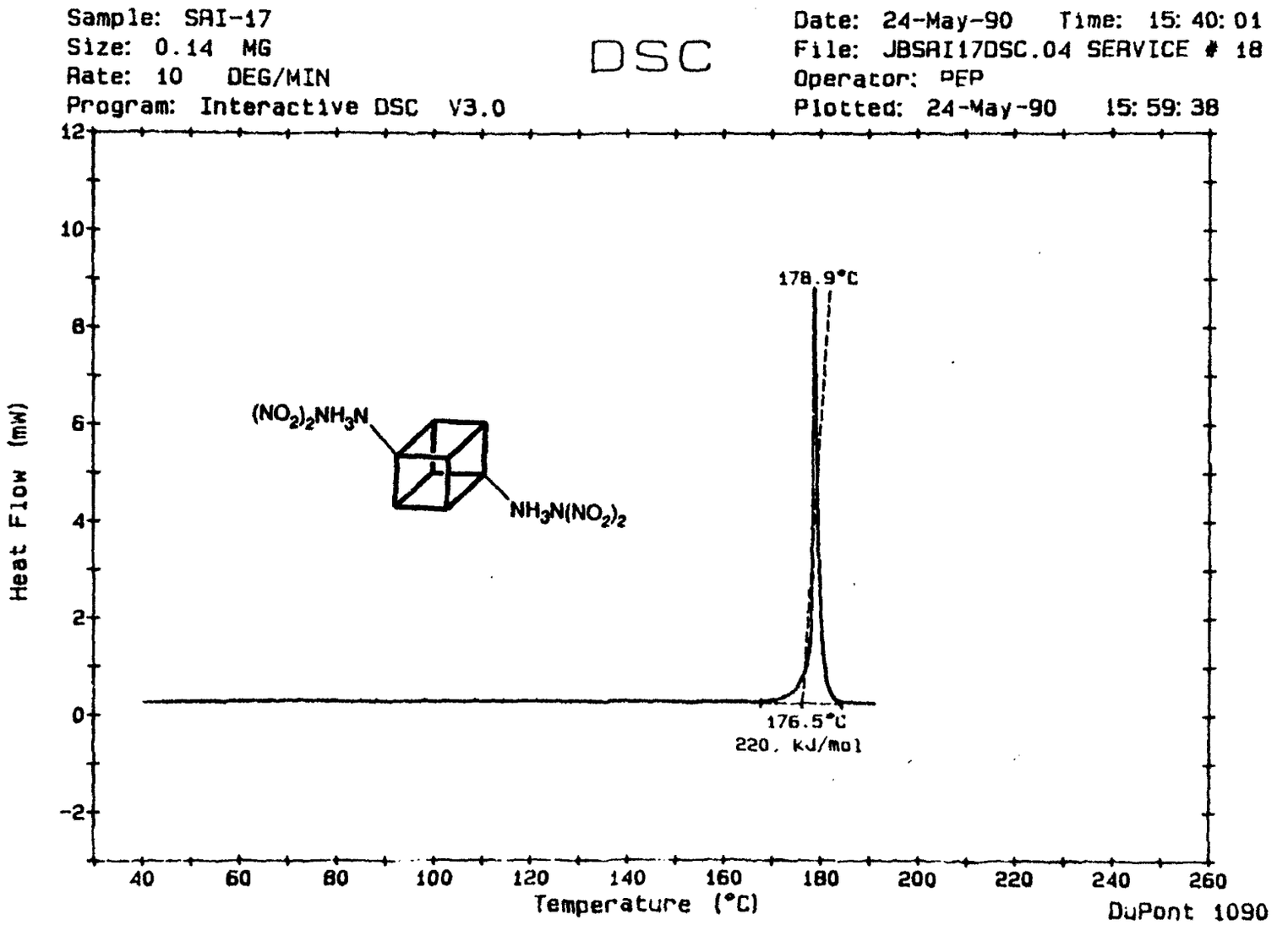


Figure 25. DSC of cubane-1,4-bis(ammonium dinitramide).

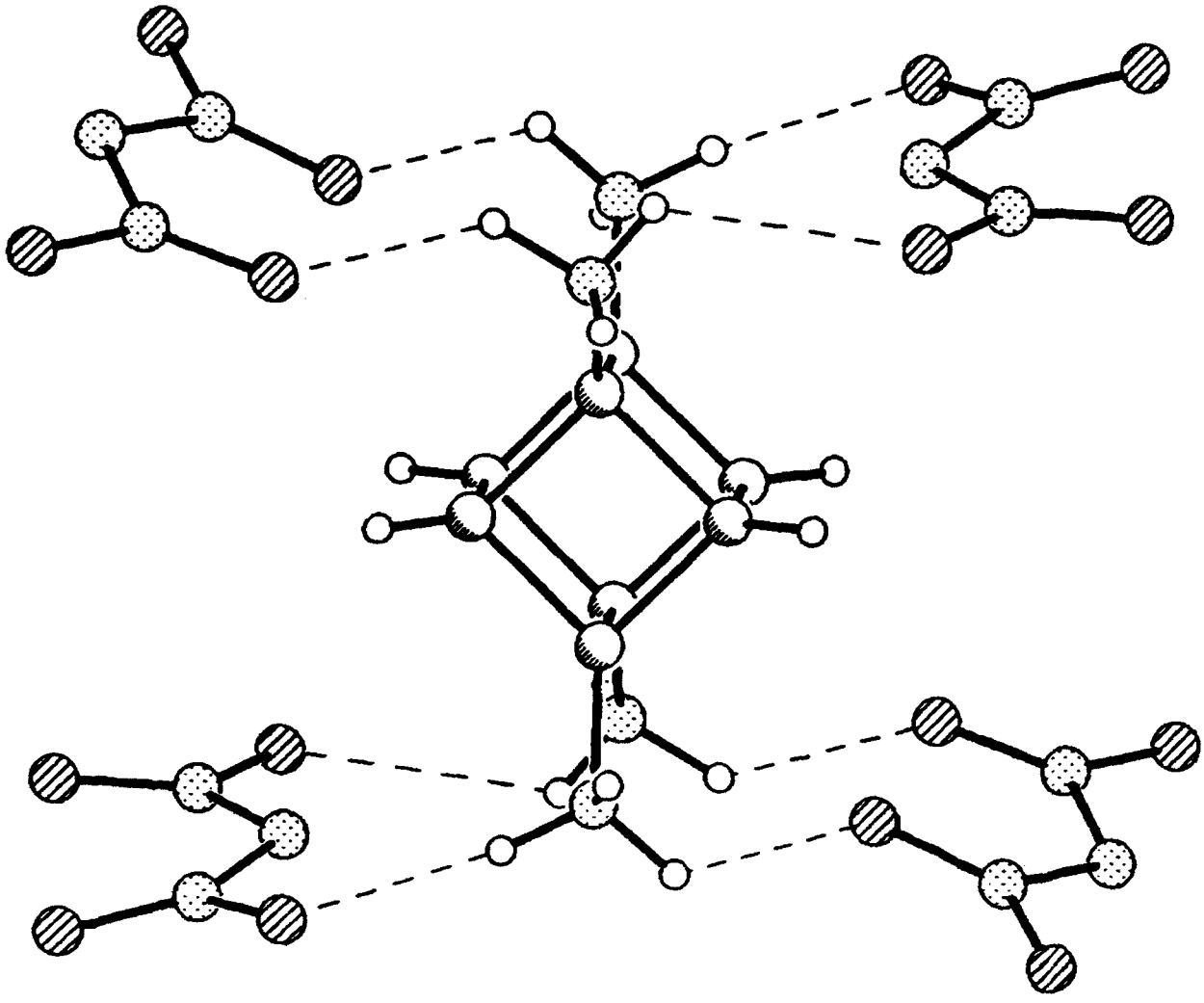


Figure 26. Crystal structure of cubane-1,2,4,7-tetrakis(ammonium dinitramide).

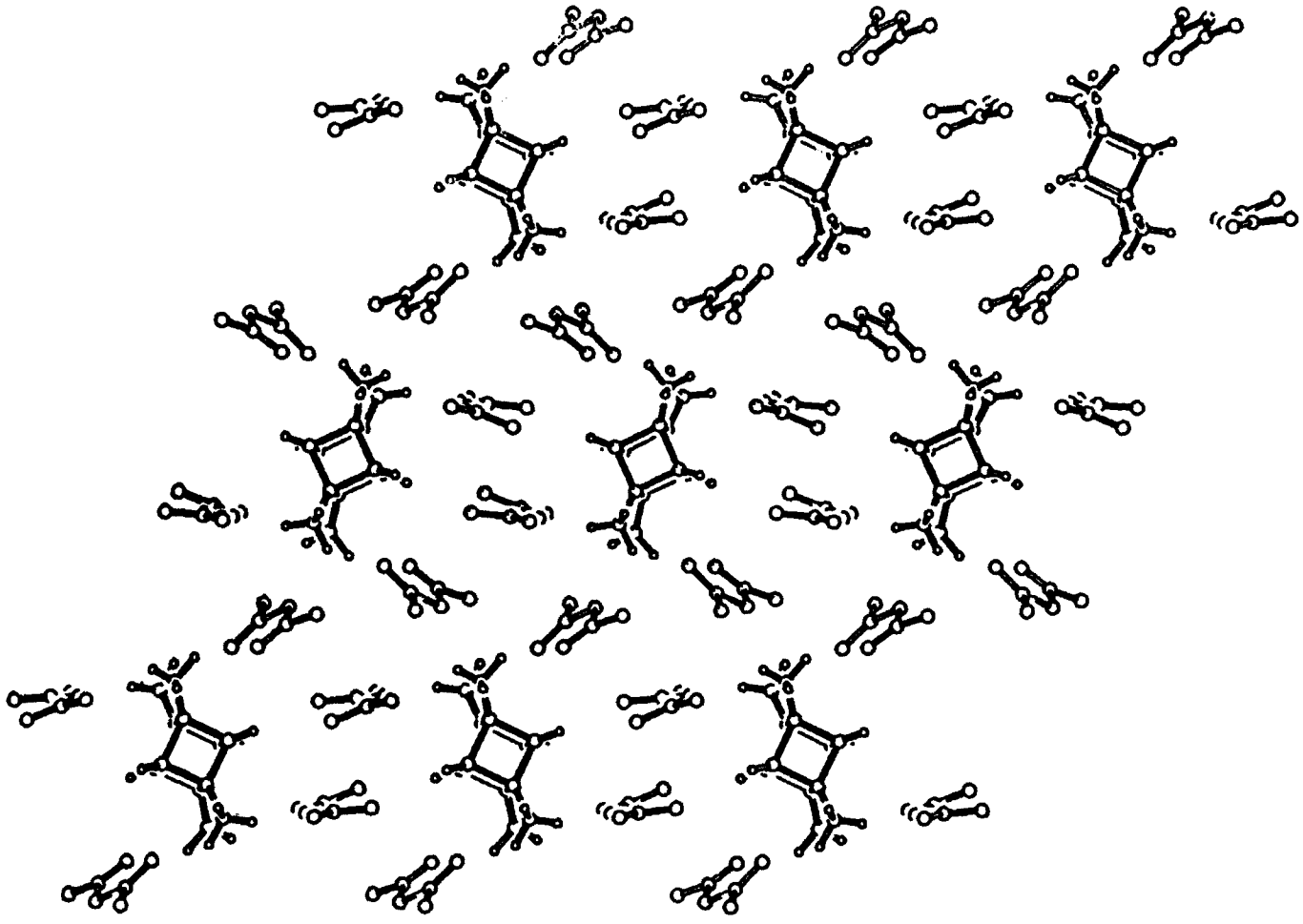


Figure 27. View of crystal lattice of cubane-1,2,4,7-tetrakis(ammonium dinitramide).

positive because of the presence of the cubane, but no heat of formation has been measured to date.

The thermal properties of cubane-1,2,4,7-tetrakis(ammonium dinitramide) are again unusual, as seen in Figure 28. The compound shows no melting point, but the onset for thermal decomposition is now around 135°C and thus appears to be dominated by the presence of the dinitramide ions in the crystal lattice.

Acid and Base Stability of Dinitramide Salts

Under this program, we have been able to make several preliminary observations on the acid/base stability of dinitramide salts. We have not performed extensive studies of the acid/base properties of dinitramides, but we report here our preliminary observations on their stability. The proposed mechanisms are speculative, based on the products observed.

In general, we have found dinitramides to be stable to concentrated base. For example, cesium dinitramide is stable to decomposition in 12 M NH_4OH at room temperature. We have not had time to investigate its stability at higher temperatures or with other bases.

The situation in acids, however, is considerably different. We have observed that even traces of acid will catalyze the decomposition of dinitramide salts over time. The primary decomposition products are nitrate and presumably N_2O (not determined spectroscopically, but rather inferred from the likely decomposition pathways shown in Scheme 6 below). The rate of acid catalyzed decomposition increases directly with acidity. In sulfuric acid, decomposition is quite rapid in 18 M (concentrated) H_2SO_4 and slower at lower acid concentrations. Spectral changes are observed in the uv/vis between 10 M and 12 M H_2SO_4. Between 10 M and 12 M H_2SO_4, the dinitramide absorption at 284 nm is significantly reduced. We interpret this finding to indicate that a protonation of the dinitramide ion is occurring over this acid range, giving $HN(NO_2)_2$. At lower concentrations the compound exists as the separated ion pair $M^+/N(NO_2)_2^-$ in solution. Dilution of these concentrated acid solutions returns the uv/vis to its original form, by converting the acid form to the separated ion pair (when we allow for the dilution effects and some decomposition of the dinitramide caused by the acid). Table 3 lists our preliminary measurements on the rate of decomposition of dinitramide ions in sulfuric acid over the range 11 to 13 M.

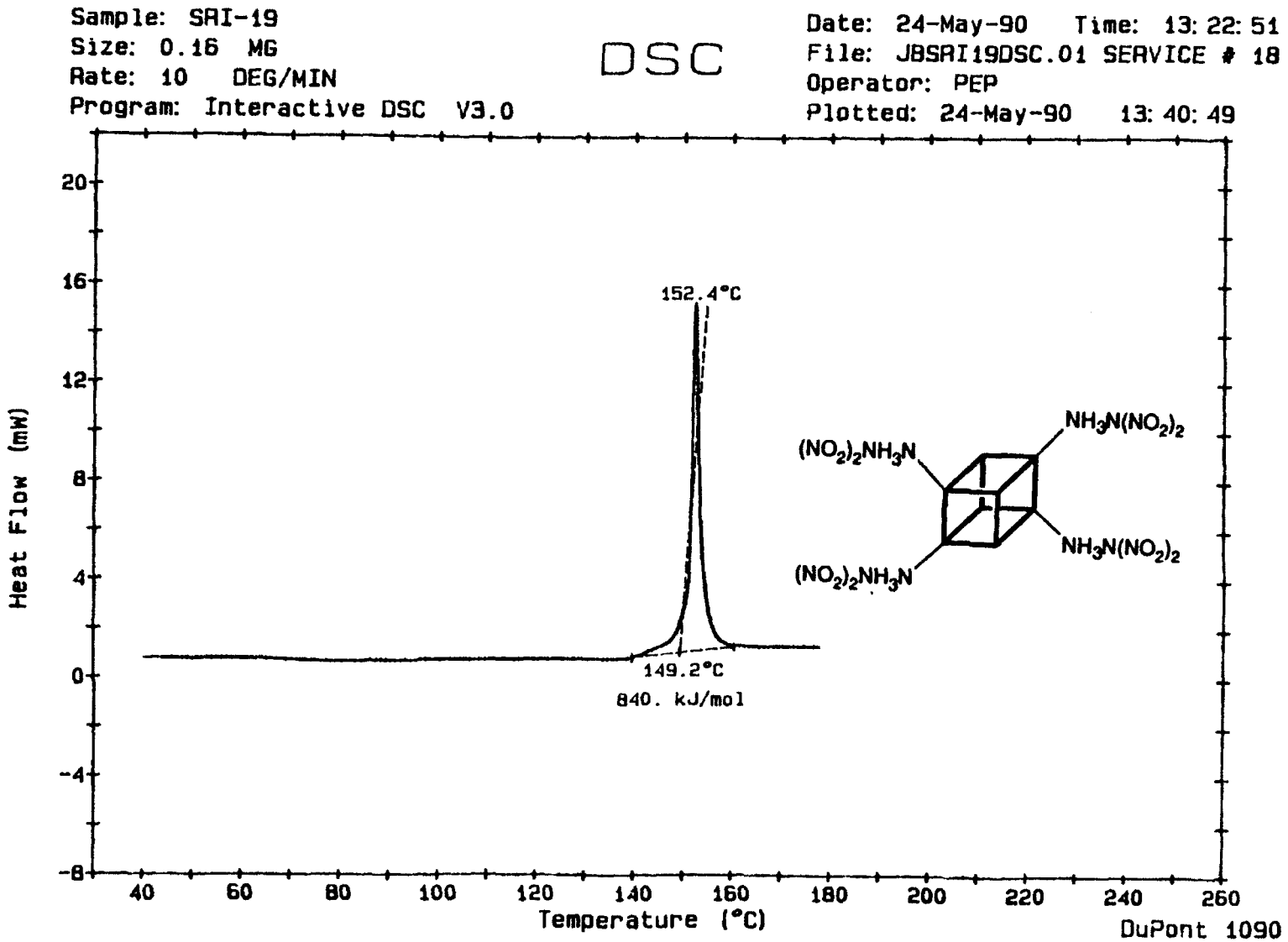


Figure 28. DSC of cubane-1,2,4,7-tetrakis(ammonium dinitramide).

Table 3

PRELIMINARY MEASUREMENTS OF THE DECOMPOSITION OF $CsN(NO_2)_2$ IN H_2SO_4 AT ROOM TEMPERATURE

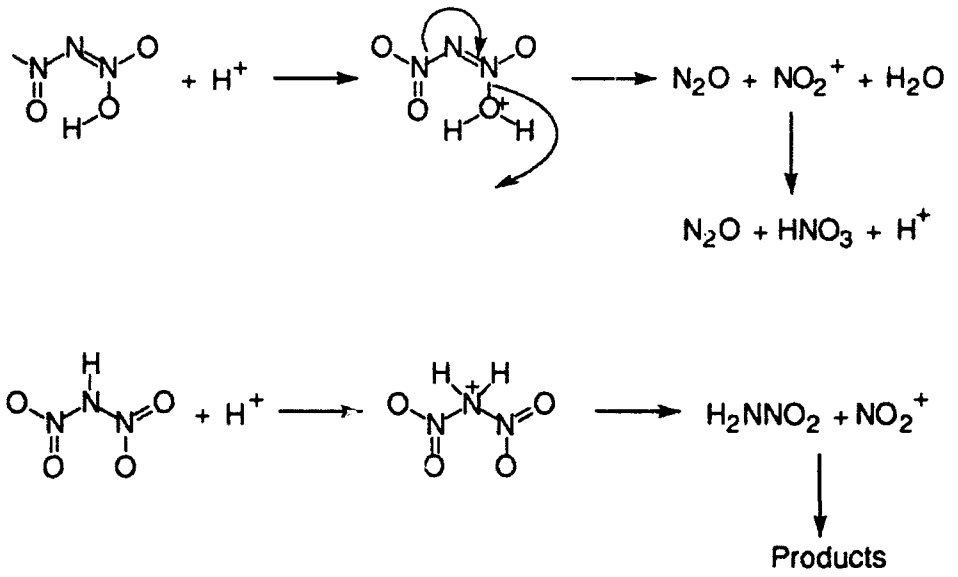
Sulfuric Acid Concentration (Molarity)	$k(min^{-1})$	$t_{1/2}$ (min)
11.0	0.00742	93
12.0	0.0252	28
13.0	0.335	2.1

As one would expect for an acid catalyzed reaction, the rate of decomposition increases with the acidity. The plots of the decomposition of dinitramide show a first-order decomposition. The rate of decomposition increases with increasing acid concentration.

We speculate that decomposition of dinitramide occurs upon the second protonation of the anion, as shown in the mechanisms in Scheme 6. Protonation can occur at either the oxygens or the central nitrogen. Protonation on the oxygen should follow the mechanism below with initial elimination of nitrous oxide, nitronium ion, and water. This mechanism is consistent with the observed products of decomposition. We can not distinguish the first route from the second proposed decomposition pathway, where the protonations occur at the central nitrogen. We favor the first route (with protonation at oxygen), since the electron densities on the nitro groups would tend to indicate that this route would be favored. The decomposition products in either case should be the same and further studies are required to distinguish these routes.

The mechanisms proposed above do not explain the production of a small quantity of nitrite ion as an observed decomposition product of dinitramide. To date, there is no good mechanistic explanation for nitrite production. We speculate that nitrite is formed by a nitro-nitrite rearrangement that then cleaves to give NO^+, which then reacts with water to give nitrous acid(a source of nitrite ion) and a proton.

The situation is somewhat different in nitric acid. Nitric acid has the possibility that lower oxides of nitrogen can be present. We have observed that the lower oxides of nitrogen enhance the rate of decomposition of dinitramide, presumably by one-electron oxidation. We have conducted preliminary investigations where we measured the rates of decomposition of cesium dinitramide in nitric acid both in the presence and absence of lower oxides.



Scheme 6. Acid catalyzed decomposition of dinitramide ion

Cesium dinitramide in a solution of 70% nitric acid without purification has a $t_{1/2}$ = 3 hours, but when the nitric acid by addition of a small amount of urea[4] the $t_{1/2}$ increases to 14 hours. Thus, the rate of decomposition of dinitramide in nitric acid is significantly slowed by removal of NO^+ or NO_x species from nitric acid solutions, which indicates that the primary decomposition route in nitric acid is via a one-electron oxidation route rather than an acid catalyzed decomposition. The results of this preliminary study are summarized in Table 4 below.

As can be seen from these measurements, the rate of reaction is significantly reduced when urea is added to decompose the lower oxides of nitrogen. The lifetime of dinitramide under these conditions is about 4.8 times as long as in the samples where the lower oxides were still present. The results with 90% nitric acid show the dramatic enhancement of the rate of decomposition of dinitramides as the acid concentration is increased.

[4] L. F. Fieser, and M. Fieser, *Reagents for Organic Synthesis*, Vol. 1 (John Wile and Sons, Inc., New York, 1967), p. 733; J. P. Freeman and I. G. Shepard, in *Organic Synthesis: Collected Volume V*,.H. E. Baumgarten, Ed. (John Wiley and Sons, Inc., 1973), pp. 839-842.

Table 4

PRELIMINARY MEASUREMENTS OF THE DECOMPOSITION OF $CsN(NO_2)_2$ IN HNO_3 AT ROOM TEMPERATURE

Nitric Acid Concentration (%)	$k(hr^{-1})$	$t_{1/2}$ (hr)
70	0.228	3.04
70	0.048	14.4
90	1.81	0.38

*Urea added to eliminate NO_x.

EXPERIMENTAL

Synthesis of Hexahydro-1,3,5-tris(methanesulfonyl)-1,3,5-triazine (1)

N, N-bis(trimethylsilyl)methanesulfonamide, 1 g (~ 4 mmol), was dissolved in 10 mL of EtOAc and treated with 4 mmol of $CH_2(OCH_3)_2$ followed by ~50 mg of Me_3Si-SO_3CF_3. A mild exotherm ensued, and after 30 minutes a fine precipitate was observed. After 3 hours, the solution was filtered, giving a mass of 350 mg. Sublimation (320°C/0.1 torr) gave 100 mg of crystals. ^1H NMR (CF_3SO_3H) ∂ 3.6. Mass spectrometry (FIMS) m/e 321, as expected.

Attempts to Convert 1 to RDX

All attempts to convert compound 1 to RDX by reaction with NO_2BF_4 or in mixed sulfuric/nitric acids gave either unreacted starting material or, if the reaction was heated, no product at all. Available evidence indicates that compound 1 is more stable to acid that RDX.

Synthesis of N-(diphenylphosphine)-N,N-trimethylsilylamine (4)

$LiN(SiMe_3)_2$, 50 mmol, was formed in 100 mL of anhydrous ether by treating $HN(SiMe_3)_2$ with 55 mmol of n-butyl lithium. The resulting solution was cooled to -78°C (giving a precipitate) and then treated with 50 mmol of Ph_2PCl. The reaction was slowly warmed to room temperature (25°C), diluted with hexane, decanted, concentrated, and then distilled. The yield was 12, (75%,, Bp 140°C at 0.1 torr, a clear, pale yellow oil. ^1H NMR ($CHCl_3$) ∂ 0.2 (s, 9H), ∂ 7.3-8.0 (m, 10 H).

Synthesis of N-(diphenylthiophosphate)-N,N-trimethylsilylamine (5)

Phosphine (3.4 g, 10 mmol) was treated (neat) with 320 mg (10 mmol) of S_8. A gentle exotherm ensued. To hasten reaction, heat was applied with an inert argon atmosphere present. The sulfur dissolved and the product crystallized out as a solid, giving a quantitative yield. ^1H NMR ∂ 0.1 (s, 9 H), ∂ 7.2-8.2 (M, 10 H).

Synthesis of Hexahydro-tris(N,N',N''-diphenylthiophosphoryl)-1,3,5-triazine (6)

Compound 5, 10 mmol, was mixed with 10 mmol of dimethoxy methane in 15 mL of ethyl acetate. Trimethylsilyl triflate (~1 mmol, 200 mg) was added slowly in cresol. Stirring was continued for 3 days. From this mixture, 1.1 g of fine white crystals was isolated. ^{1}H NMR ($CHCl_3$) ∂ 4.2(+, 6 H, J = 8 Hz), ∂ 7.2-8.2 (m, 30 H). Mass spectrometry (FIMS) m/e 735 and 367, as expected.

Synthesis of Glyoxal *tetra*ethylacetal [alternatively, 1,1,2,2-tetra-(n-butylether)ethane], Compound (7)

Ethanol (3 mol), glyoxal (0.5 mol of 40% aqueous solution, or 75 g of glyoxal), benzene (1 L), and H_2SO_4 (1 g) were mixed and refluxed with a Dean-Stark trap until H_2 evolution ceased (8 hours). The reaction was washed with 1 x 100 mL of 5 M NaOH, concentrated, and then distilled. Its boiling point was 45-50°C at 0.1 torr. The yield was 60 g.

Synthesis of *meso*-1,2-(n-butylether)-1,2-(N-trimethylsilyl-N-methansulfonate)ethane (8)

Compound 7 (2 mmol, 600 mg) was mixed with N,N-bis(trimethylsilyl)-N-methanesulfonamine (4 mmol, 1 g) neat at room temperature, and 50 mg of $Me_3Si\text{-}SO_3CF_3$ was added as a catalyst. A slow, gentle exotherm ensued, and after 1 day a solid had precipitated; this solid was collected and crystallized from dry ethyl acetate. The yield was 400 mg (~35%). ^{1}H NMR ∂ 1.0 (s), ∂ 1.3-1.4 (d), ∂ 1.6-2.8 (m), ∂ 3.9 (s), ∂ 4.1-4.8 (m), ∂ 5.9 (s), ∂ 6.1 (s). Integration did not yield integral quantities.

Synthesis of (9)

Compound 8, 180 mg, $CH_2(OCH_3)_2$, and ~10 mg of $Me_3SiSO_3CF_3$ were dissolved in 2 mL of $CHCl_3$ and warmed to 45°C for 3 days. The volatiles were removed under vacuum yielding 100 mg of crude product. From this product a crude NMR was run. ^{1}H NMR($CDCl_3/CHCl_3$) ∂ 0.7-1.7 (m), ∂ 2.1(s), ∂ 3.0 (s), ∂ 3.5-4.3 (m); ∂ 4.8(s), ∂ 5.1(s), ∂ 8.9 (m)-integration was nonintegral. TLC showed three spots ($EtOAc/SiO_2$) R_f = 0.5, 0.6, 0.7.

Synthesis of Clathrate of CL-20 and HN_3 (SRI-4)

CL-20, 108 mg, was dissolved in 1 g of ethyl acetate, diluted with 3 g of ethanol, and then treated with 2.0 g of Me_3SiN_3. This mixture was allowed to stand for 5 minutes, at which point the exotherm had completely subsided. Next 8 g of $CHCl_3$ was added and the solution was allowed to stand at room temperature for 5 hours and then, filtered, which gave 95 mg of diamond shaped crystals. X-ray analysis showed the presence of 2 CL-20 to 1 HN_3 in the crystal lattice.

Synthesis of Clathrate of CL-20 and H_2O_2 (SRI-5)

A solution of 2 g EtOH, 0.5 g 90% H_2O_2, 0.8 g triethyl orthoacetate, and 1.0 mg of CH_3SO_3H was prepared and allowed to stand for 1 hour at room temperature. A solution of 67 mg of CL-20 in 200 mg of ethyl acetate was mixed with 1 g of the above described solution and the mixture diluted with 5 g of $CHCl_3$. After 48 hours, prismatic, square, and hexagonal crystals precipitated with a yield of 40 mg.

Synthesis of Clathrate of CL-20 and NH_2OH (SRI-20)

CL-20, 100 mg, was dissolved in 1 g of ethyl acetate, diluted with 1.6 g of ethanol, and then treated with 100 mg of NH_2OH. A crop of hexagonal and rhombic crystals precipitated, the total mass being 30 mg.

Synthesis of 1-(N,N-dinitramino)-2-trimethylsilylethane

To form a 2-(trimethylsilylethyl)-N,N-dinitramine precursor, an ice-cooled mixture of 1.45 (11 mmol) of nitronium tetrafluoroborate, 10 mL of acetonitrile, and 700 mg (11 mmol) of 99+% HNO_3 (under argon) was formed, and then 10 mmol of 2-(trimethylsilylethyl)isocyanate was added, with fume-off avoided by controlling the rate of addition as appropriate. The reaction was stirred for 15 minutes at O°C, diluted to 25 mL with $CHCl_3$, and filtered rapidly through a 1 x 3 inch plug of SiO_2, eluting with 100 mL of $CHCl_3$. Chromatography of the crude product, by eluting $CHCl_3$ over SiO_2 and collecting the fastest-moving, uv-active material ($R_f = 0.5$), resulted in collection of 500 mg of the desired 2-(trimethylsilylethyl)-N,N-dinitramine precursor, about a 25% yield.

Synthesis of Cesium Dinitramide (SRI-11)

About 2.5 mL of 2-(trimethylsilylethyl)-N,N-dinitramine, such as formed above, was dissolved in 20 mL of acetonitrile and maintained at 20° C. To this solution was added 1 g of cesium fluoride. The solution was stirred for about 120 minutes. The cesium N,N-dinitramide salt product was then recovered by crystallization from ethyl acetate and acetonitrile. The product yield was 900 mg, or about a 50% yield.

Synthesis of Tetramethylammonium Dinitramide

About 2.5 mL of 2-(trimethylsilylethyl)-N,N-dinitramine, such as formed above, dissolved in 20 mL of acetonitrile and maintained at 20 °C. To this solution was added 1 g of tetramethylammonium fluoride. The solution was stirred for about 120 minutes. The tetramethylammonium N,N-dinitramide salt product was then recovered by crystallization from ethyl acetate. The product yield was 900 mg, or about a 50% yield.

Synthesis of Other Dinitramide Salts by Ion Exchange

All desired dinitramide salts can be prepared by ion exchange starting from cesium dinitramide and using AMBERLYST 15 Sulfonic Acid Resin charged with the appropriate cation: Elution is performed using a methanolic solution of cesium dinitramide over a large excess of the charged resin.

In a typical example, 10 g of AMBERLYST 15 (sulfonic acid resin) was suspended in 100 mL of CH_3OH, treated with 5 mL of 95% hydrazine, filtered, and washed with 100 mL of CH_3OH. This 10 g of material was then placed into a 4 x 0.5 inch column and eluted with at solution of 200 mg of cesium dinitramide in 5 mL of CH_3OH, followed by washing with an additional 20 mL of CH_3OH. Concentration of the effluent gave approximately 100 mg of pure hydrazinium dinitramide (SRI-13) after crystallization from CH_3CN. **This material is shock sensitive and one should exercise caution in handling it.**

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ACKNOWLEDGEMENTS

We thank Drs. Richard Miller, Judah Goldwasser, and William Koppes of the Office of Naval Research (Contract No. N00014-86-C-0699) for support of this work. We thank Drs. Richard Gilardi, Judith Flippen-Anderson, and Clifford George of the Structure of Matter Laboratory, Naval Research Laboratory, for the x-ray crystal structure determinations and the stimulating discussions, which made it possible to progress much faster than would otherwise have been possible.

Appendix A

SYNTHESIS OF ENERGETIC CLATHRATES

SYNTHESIS OF ENERGETIC CLATHRATES*

By: and R. J. Schmitt†, J. C. Bottaro, and P.E. Penwell,
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Innovative concepts in materials design must be explored to achieve the goal of generating more propulsion or explosive power in less volume. Recent synthesis advances have resulted in the synthesis of HNIW. Yet improvements are highly desirable. A promising way to improve this new material would be to combine or modify its properties by preparing a clathrate using HNIW as the host molecule. Synthesis of clathrate compounds from HNIW or existing energetic compounds would have two great advantages: (1) It would be a straightforward method for improving these existing materials without requiring a "start from scratch" synthesis of new energetic compounds, and (2) this combination of energetic materials may result in materials with improved properties such as reduced sensitivity to friction, heat, or shock.

The early determinations of crystals of HNIW showed that water molecules were incorporated into the crystal lattice in such a manner as to give a HNIW/water clathrate. Clathrates are formed when the "guest" molecule in the crystal lattice is completely enclosed by the "host" molecule on a molecular level. Thus the guest has no means of escape and is incorporated into the crystal lattice until either the clathrate is recrystallized to release the guest or the crystal lattice destroyed. We present definitions of terms to minimize confusion.

Clathrate: A crystal having completely enclosed cavities, thus imprisoning guest molecules within the cavity.

Host: A molecule that forms a crystal lattice with spaces large enough for the guest.

Guest: A molecule incorporated into the crystal structure of the host.

Inclusion Compound: Any crystal composed of a guest and a host.

Channel Complex: A crystal having long tunnels, layers, or channels that extend from the interior through to the surface of the crystal.

We believe that the synthesis of energetic clathrates and complexes can potentially result in the following benefits:

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*This work was performed under Contract No. N0001114-88-C-0537 with the Office of Naval Research.
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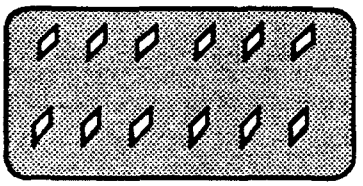
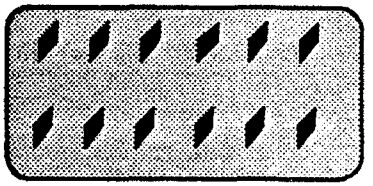
- New classes of energetic materials having modified properties.
- Higher energy density due to filling empty interstitial cavities of crystals with either oxidizers or fuels.
- Molecular level doping for burn rate modifiers.
- Introduction of molecular level shock absorbers, resulting in decreases in sensitivity.
- Use of existing energetic materials.
- Stabilizer incorporation at the molecular level to give increased shelf life of energetic materials due to suppression of degradative reactions.

Potential performance improvements from clathrates would result from filling the interstitial voids or cavities with a fuel, a burn rate modifier, or more oxidizer. Such voids lower the density and reduce the energy density of the ingredient. In essence, the approach is to use oxidizer as a host for a guest molecule incorporated into the crystal structure to create a clathrate or an inclusion complex.[1,2] This approach allows the incorporation of burn rate modifiers and other additives at the molecular level, where they would do the most good, that is, intrinsically incorporated into the crystalline structure of the oxidizer and not present in the formulation as a lump at some distance from the oxidizer. We also envision the possibility of one of the components of the clathrate acting as a molecular level shock absorber. The guest can absorb some of the energy of a shock through hydrogen bonds just as the hydrogen bonding operates in TATB to dramatically reduce its shock sensitivity. Thus, hydrogen bonding within the materials acts as a form of molecular insulation, minimizing repulsions or frictional forces between energetic molecules. We show this concept graphically below.



Less energy dense crystal with unfilled cavities



Higher energy, dense crystal with filled cavities

The observation of water clathrates led to our studies on the preparation of clathrate molecules designed to increase the energy content of crystalline explosives or propellants. Our work was not the first attempt at the synthesis of clathrates or inclusion complexes of explosives, although it appears to be the most successful in terms of increasing the energy content. Initial efforts were made in the late 1950s by Nagle,[3] with no apparent success in synthesizing a useful material. More successful work was done in the late 1960s by George et al.[4] and in the early 1970s by Claringbull and Small[5] on monosolvates of HMX and BSX, respectively. These last two groups both focused on attempts to prepare monosolvates of the energetic materials. Large guest molecules were generally used, including molecules such as DMSO, DMF, acetophenone, and NMP. The guest chosen for these studies resulted in observable increases in energy content; indeed, the focus of the studies was to study the monosolvates, not to develop a higher energy content for these materials. More recently, a significant amount of work has been done at the

Naval Weapons Center (NWC), China Lake, by Dr. Mae Chan on preparing inclusion complexes of the HNIW molecule. Her work demonstrated that a range of compounds can be co-crystallized with HNIW. Overall, this work demonstrates that quite a range of co-crystals can be prepared using a range of guests. The success of Chan et al. in preparing these compounds with multiple guests bodes well for this program.

We have demonstrated the synthesis of energetic clathrates by preparing the first energetic clathrate of the HNIW system. This clathrate is composed of 2 HNIW to 1 HN_3. The resulting crystal has a higher density than some crystal forms of HNIW, crystallizes faster than HNIW alone in the same environment and yields a higher quality crystal, and appears (from our initial tests) to have the same or better shock sensitivity in preliminary tests. The x-ray data show the HN_3 sealed in a crystal having a stoichiometry of 2 HNIW to 1 HN_3 (SRI-4, Figure 1), and the HN_3 cannot be removed from the crystal even under high vacuum; thus we have a clathrate of HNIW and HN_3. We have synthesized a true clathrate. A DSC of SRI-4 (Figure 2) shows thermal behavior similar to that of pure HNIW. The onset for thermal decomposition can be seen to occur at around 200°C.

TABLE 1: Clathrate Compounds

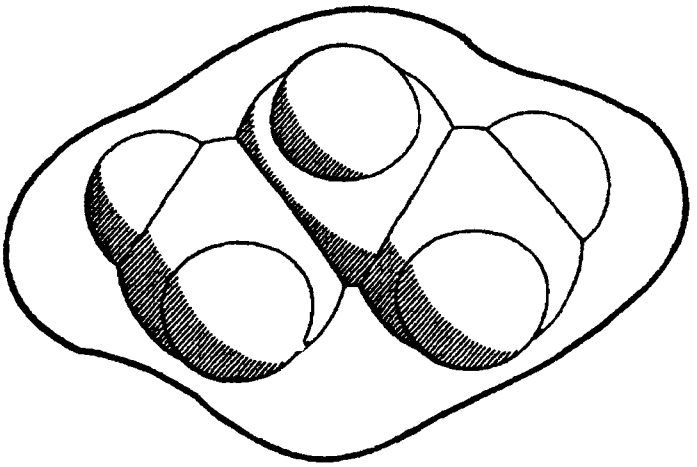
Guest	Result
NH_3	Decomposes
HN_3	Crystal obtained (SRI-4) Stoichiometry of 2 XXX to 1 HN_3
H_2O_2	Crystal obtained (SRI-5) Stoichiometry of 2 XXX to 1 H_2O_2
NH_2OH	Crystal obtained (SRI-20) Stoichiometry of 2 XXX to 1 NH_2OH

Two other clathrates have been prepared and had their x-ray crystal structures determined to date. They are SRI-5 (2 HNIW to 1 H_2O_2) and SRI-20 (2 HNIW to 1 NH_2OH; see Figure 3). The thermal analysis (TGA) of SRI-5 is shown in Figure 4. At approximately 160°C a loss of 3.86% of the material is observed, which this corresponds to the H_2O_2 within the sample decomposing and being lost as the sample is slowly heated. SRI-20 was prepared to test the ability of the hydroxylamine to desensitize HNIW. A sample of SRI-20 was provided to Mr. Clifford Coon at Lawrence Livermore National Laboratory (LLNL), who compared the shock sensitivity of SRI-20 to that of pure HNIW. Within the sensitivity of the instrument the sensitivity of the clathrate and pure material were observed to be the same. Thus, at least for this clathrate, no gross desensitization was observed.

In our initial experiments, we tried to prepare clathrates of HNIW having ammonia as the guest, but these experiments were unsuccessful. We believe the reason these guests failed is that the ammonia reacted with HNIW to decompose the HNIW molecule, presumably through a proton abstraction reaction caused by the high basicity of the ammonia. This reaction had not been observed previously and is new chemistry for HNIW.

One of us (RG) studied the crystal packing of HNIW and the HNIW/HN_3 crystal. He determined the size of the void in HNIW and modeled several possible guests in HNIW. Figure 5 shows a space-filling model of HN_3 in a cage of four HNIW molecules (the top two HNIW molecules are left off for clarity). The cavity in which the HN_3 sits is clearly visible. The H atom

on the HN_3 is hydrogen bound to the surrounding HNIW molecules and is not shown in these views. The model of a space-filling propane molecule inside the cavity formed by the surrounding HNIW molecules is shown below to give a feel for the size of the cavity.



Modelling of the cavity shows that it is large enough to enclose a propane or perhaps a larger guest molecule. The properties of the cavity are summarized below:

- HNIW crystal cavity size is flexible; it "breathes" to accommodate different guests.
- Unit cell is 0.2 Å larger when HN_3 is enclosed than when H_2O is enclosed; however, the density increases.
- Cavity size with HN_3 is approximately 5.8 x 5 x 2.1 Å, large enough to accommodate 2 H_2Os, a propane, or other compounds having 3 heavy atoms.

The observation that the size of the crystal unit adjusts to accommodate different hosts is significant. This observation implies an inherent flexibility in the crystal structure, which would allow many alternative guests to be considered. Finally, new crystalline forms are likely to occur with some guests as the crystal structure adjusts to accommodate the guest, including perhaps some crystal forms with greater density than that observed to date.

The authors thank Dr. Richard Miller and the Office of Naval Research for their support of this work and many stimulating discussions on this subject. We also thank Mr. Clifford Coon of Lawrence Livermore National Laboratory for providing us with samples of HNIW, for the sensitivity testing of SRI-20, and for discussions of the concept.

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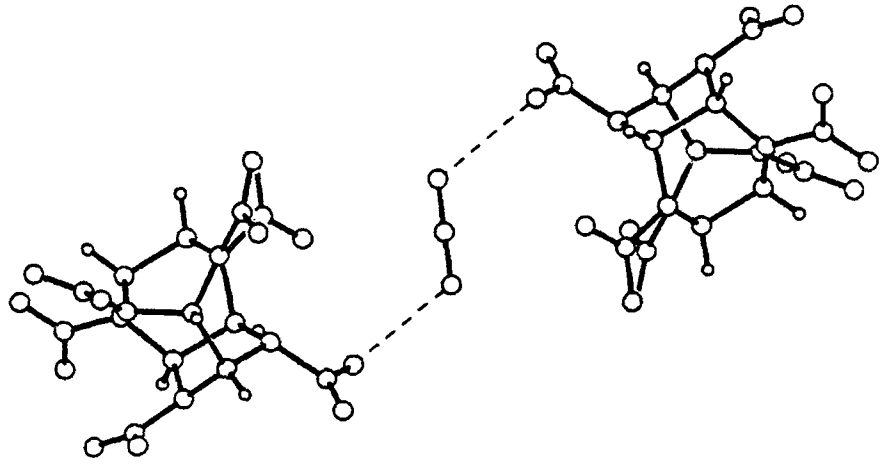

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Figure 1. SRI-4, a clathrate of 2 HNIW to 1 HN_3.

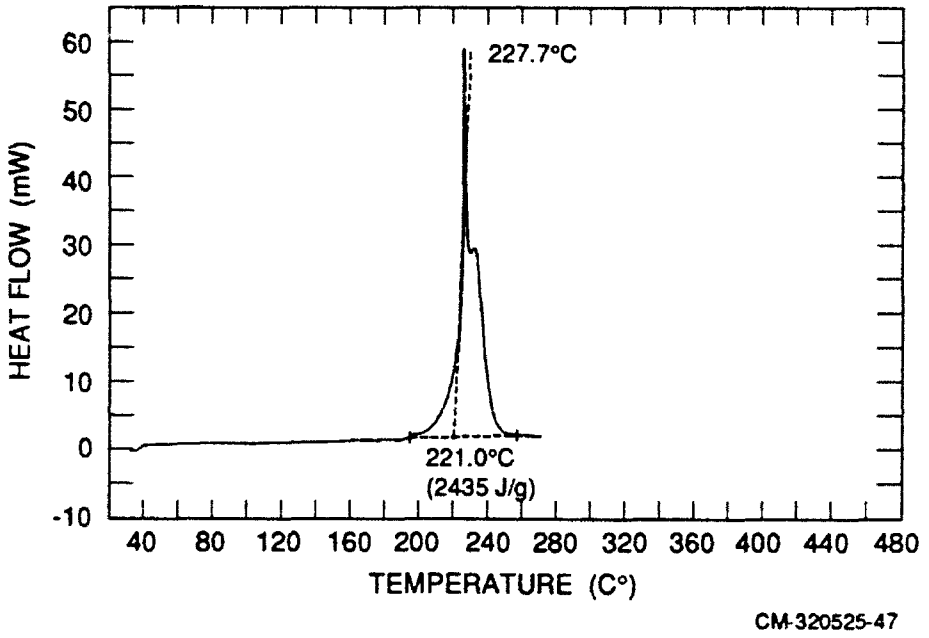

Figure 2. DSC of SRI-4.

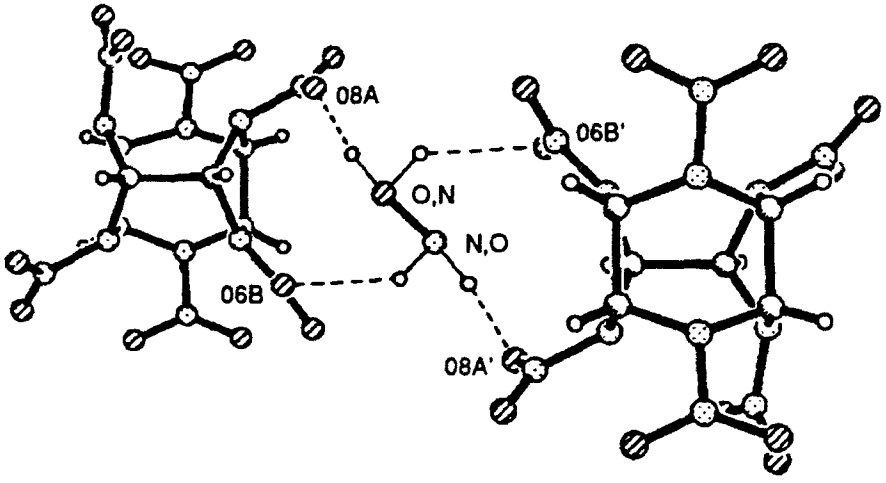

Figure 3. SRI-20, a clathrate of 2 HNIW to 1 NH_2OH.

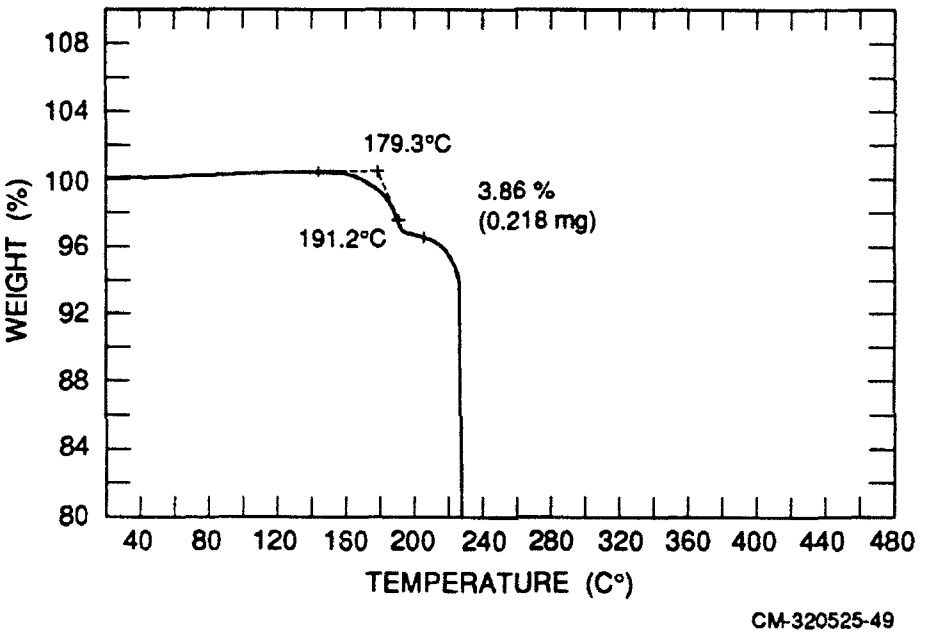

Figure 4. TGA of SRI-5 showing loss of H_2O_2 prior to decomposition of the HNIW host molecule.

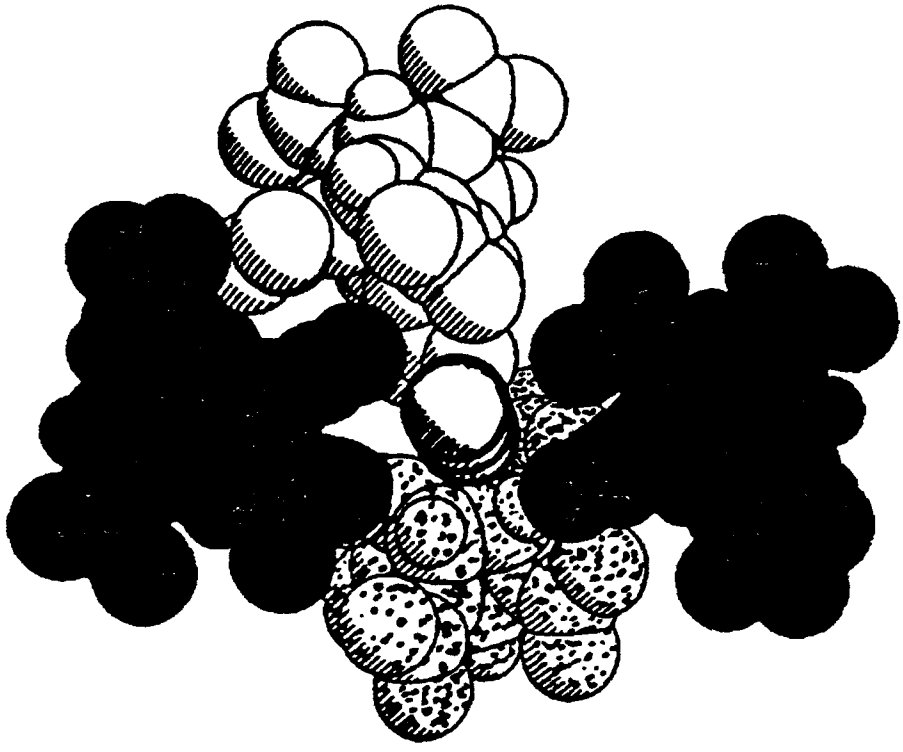

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Figure 5. View of four host molecules and a trapped azide (HN_3) guest. Two more host molecules lie above the azide and complete the cage. (R. Gilardi, NRL)

Appendix B

DINITRAMIDE SALTS AND METHOD OF MAKING SAME

(International Patent Application No. WO 91/199669)

DINITRAMIDE SALTS AND METHOD OF MAKING SAME

GOVERNMENT RIGHTS

This invention was made under government contracts N00014-86-C-0699 and N00014-88-C-0537 of the Office of Naval Research; and the government of the United States, therefore, has rights in this invention.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to dinitramide salts and a method of making same from alkyl-N,N-dinitramines.

2. Description of the Related Art

Solid oxidizers, such as ammonium perchlorate or potassium perchlorate, have been used in the past in rocket propellant formulation because of their greater stability than liquid oxidizers. However, the presence of a halogen in the solid oxidant produces a smoke trail which is observable on radar and sometimes visually as well. Also, chlorine poses a serious atmospheric environmental hazard of ozone depletion.

Because of such shortcomings in the use of perchlorate solid fuel oxidizers, other materials, including nitrate (NO_3^-) compounds, have been investigated in the search for oxidizers which would provide the desired energy density and stability, without the drawbacks of the perchlorate oxidants.

Hamel et al. U.S Patent 3,428,667 describes the reaction of an ionic nitronium salt with a primary organic nitramine to form N,N-dinitramines having the general formula $R\text{-}N((NO_2)_2)_n$ where n is 1-2 and R is a monovalent or divalent organic radical. These compounds are said to be highly energetic and useful as ingredients in propellant, explosive, and pyrotechnic compositions.

Willer et al. U.S. Patent 4,878,968 describes the formation of gun and rocket propellants which include substituted cubanes such as cubane-1,4-bis(ammonium nitrate), or 1,4-bis(ammonium)pentacyclo[$4.2.0.0^{2,5}.0^{3,8}.0^{4,7}$]octane dinitrate; and cubane ammonium nitrate, or pentacyclo-[$4.2.0.0^{2,5}.0^{3,8}.0^{4,7}$]-octylammonium nitrate.

Leroy et al., in "A Theoretical Investigation of the Structure and Reactivity of Nitrogen-Centered Radicals", published in the Journal of Molecular Structure (Theochem), 153 (1987) on pages 249-267, by Elsevier Science Publishers B.V. Amsterdam, The Netherlands, discusses the structure, stability, and reactivity of nitrogen-centered radicals. Listed in Table 6 are various reactions of N-centered radicals, including reactions of $N(NO_2)_2$ with NH_2 to form $2NHNO_2$, and with CH_3NHNO_2 to form CH_3NNO_2 and $NH(NO_2)$.

In the Third Quarterly Report on Basic Research in Solid Oxygen Oxidizers of Government Contract AF 04(611)-8549 dated December 1963, on pages 6 and 7, the reaction of nitronium tetrafluoroborate with the dianion of methylenedinitramine to form an intermediate anion is hypothesized and it is speculated

that the intermediate anion may either react with a second equivalent of nitronium tetrafluoroborate to form N,N,N',N'-tetranitromethylenediamine or undergo fragmentation to form an anion which has the formula $^{-}N(NO_2)_2$.

It would, however, be desirable to provide a stable solid ionic nitro compound useful as a rocket propellant fuel which would have the clear advantage over perchlorates of being free of chlorine, but would be as stable as presently used perchlorate compounds and be much more stable and cheaper than prior art dinitramine compounds.

SUMMARY OF THE INVENTION

It is, therefore an object of this invention to provide novel N,N-dinitramide salts having the formula $M^{+}\ ^{-}N(NO_2)_2$, where M is selected from the class consisting of a metal cation and a nitrogen-containing cation.

It is another object of this invention to provide novel N,N-dinitramide salts having the formula $M^{+}\ ^{-}N(NO_2)_2$, where M is selected from the class consisting of a metal cation and a nitrogen-containing cation having from 1 to 8 nitrogen atoms.

It is yet another object of this invention to provide novel N,N-dinitramide salts having the formula $M^{+}\ ^{-}N(NO_2)_2$, where M^{+} is a metal ion, the salt of which is capable of reacting with a nitrogen-containing compound to form the N,N-dinitramide salt.

It is still another object of this invention to provide novel N,N-dinitramide salts having the formula $M^+ N(NO_2)_2$, where M^+ is a 1-8 nitrogen-containing ion.

It is a further object of this invention to provide novel N,N-dinitramide salts having the formula $M^+ N(NO_2)_2$, where M^+ is a 1-8 nitrogen-containing ion having the formula $(R_nH_mN_z)^{+z}$, wherein n = 1 to 8, z = 1 to n, k = 0 to n+2+z, m = n+2+z-k, and each R is the same or different 1-6 carbon alkyl.

It is still a further object of this invention to provide novel N,N-dinitramide salts having the formula $M^+ N(NO_2)_2$, where M is selected from the class consisting of a nitrogen-containing cation having from 1 to 2 nitrogen atoms, such as a substituted ammonium ion, an ammonium ion, a substituted hydrazinium ion, and a hydrazinium ion.

It is yet a further object of this invention to provide a method of making N,N-dinitramide salts having the formula $M^+ N(NO_2)_2$, where M^+ is selected from the class consisting of a metal cation and a nitrogen-containing cation such as a substituted ammonium ion, an ammonium ion, a substituted hydrazinium ion, and a hydrazinium ion.

It is still another object of this invention to provide a method of making N,N-dinitramide salts having the formula $M^+ N(NO_2)_2$ by reacting a nitroamine having the formula $R_nH_mN(NO_2)_2$ with either a

metal-containing compound or a nitrogen-containing compound.

It is still another object of this invention to provide a method of making N,N-dinitramide salts having the formula $M^+ N(NO_2)_2$ by reacting a nitroamine having the formula $L_nZR'N(NO_2)_2$ with a salt having the formula MX, where n is 1 to 3, depending upon the valence of Z; L is the same or different 1-6 carbon alkyl, aryl, hydrogen, halogen, amine, or ether group; Z is an element selected from the class consisting of Si, Sn, Ge, As, B, Sb, Bi, Pb, and Hg; and R' is a 1 to 6 carbon alkylene group; the M^+ ion is selected from the class consisting of a metal cation, a substituted ammonium cation, an ammonium cation, a substituted hydrazinium cation, and a hydrazinium cation; and the X anion is an ion selected from the class consisting of fluoride, chloride, carbonate, hydroxyl, alkoxide, and carboxylate ions.

These and other objects of the invention will be apparent from the following description and accompanying flowsheet.

BRIEF DESCRIPTION OF THE DRAWING

The sole drawing is a flowsheet illustrating one embodiment of the process of the invention.

DETAILED DESCRIPTION OF THE INVENTION

The invention comprises novel dinitramide salts having the formula $M^+ \bar{N}(NO_2)_2$ which comprise stable high density, meltable, pumpable oxidizers useful as propellants in rocket engines, including stop-start rocket engines. The salts are stable up to temperatures as high as 140°C and, unlike prior art perchlorate oxidizers, do not leave smoke trails detectable visually or by radar.

In the formula for the novel dinitramide salts, $M^+ \bar{N}(NO_2)_2$, the M^+ cation may be a mono, di, or trivalent metal cation, or a nitrogen-containing cation, such as a 1-8 nitrogen-containing cation having the formula $M^+ \bar{N}(NO_2)_2$, where M^+ is an ion containing 1-8 nitrogen atoms and having the formula $(R_nH_mN_8)^{+z}$, wherein n = 1 to 8, z = 1 to n, k = 0 to n+2+z, m = n+2+z-k, and each R is the same or different 1-6 carbon alkyl.

As will be discussed in more detail with respect to the method of making the claimed dinitramide salts, metal ions which may comprise M^+ include metal ions which form soluble salts with either fluoride or chloride. Typical metals which may comprise M include alkali metals Li, Na, K, Rb, and Cs; alkaline earth metals Ca, Ba, Sr, and Mg; Group Ib metals Cu, Ag, and Au; Group IIb metals Zn, Cd, and Hg; Group III metals Al, Sc, Y, Ga, In, and the Lanthanide elements (57-71); Group IV metals Ti, Zr, Hf, Ge, and Sn; Group V metals V, Nb, and Ta; Group VI metals Cr, Mo, and W; Group VIIa metals Mn, Tc, and Re; and Group VIII metals Fe, Co, Ni, Ru, Rh,

Pd, Os, Ir, and Pt. Of the foregoing metal ions, Li, Na, K, Be, and Mg are preferred metal ions for the dinitramide salts of the invention.

When the M^+ ion is a 1-2 nitrogen-containing cation, it may have the formula $R_kH_mN_n^+$, wherein n = 1 to 2, k = 0 to 3+n, m = 3+n-k, and each R is the same or different 1-6 carbon straight chain or branched alkyl. Examples of such ions include NH_4^+, $CH_3NH_3^+$, $(CH_3)_2NH_2^+$, $(CH_3)_3NH^+$, $(CH_3)_4N^+$, $C_2H_5NH_3^+$, $(C_2H_5)_2NH_2^+$, $(C_2H_5)_3NH^+$, $(C_2H_5)_4N^+$, $(C_2H_5)(CH_3)NH_2^+$, $(C_2H_5)(CH_3)_2NH^+$, $(C_2H_5)_2(CH_3)_2N^+$, $(C_3H_7)_4N^+$, $(C_4H_9)_4N^+$, $N_2H_5^+$, $CH_3N_2H_4^+$, $(CH_3)_2N_2H_3^+$, $(CH_3)_3N_2H_2^+$, $(CH_3)_4N_2H^+$, $(CH_3)_5N_2^+$, etc.

The M^+ ion may also comprise a cubane-1,4-bis ammonium ion, such as described in the aforementioned Willer et al. U.S. Patent 4,878,968, cross-reference to which is hereby made; a cubane-1,2,4,7-tetra ammonium ion; a cubane-1,3,5,7-tetra ammonium ion; a cubane-1,2,3,4,-tetra ammonium ion; a cubane-1,2,3,4,7-penta ammonium ion; or a cubane-1,2,4,6,8-penta ammonium ion.

Other nitrogen-containing cations which may comprise M^+ include guanidium ($C(NH_2)_3^+$); triaminoguanidinium ($C(N_2H_3)_3^+$); nitronium ($O=N=O^+$); nitrosonium ($N\equiv O^+$); and a 1-10,000 nitrogen polymer of ethyleneimine.

a. <u>First Method of Preparing Dinitramide Salts</u>

The dinitramide salts of the invention may be formed, in one embodiment, by a reaction of a dinitramine having the formula $L_aZR'N(NO_2)_2$ with a

metal-containing compound or a nitrogen-containing compound such as ammonia, hydrazine, or a salt having the formula MX, where n is 1 to 3, L is the same or different 1-6 carbon alkyl, aryl, hydrogen, halogen, amine, or ether group, Z is an element selected from the class consisting of Si, Sn, Ge, As, B, Sb, Bi, Pb, and Hg; and R' is a 1 to 6 carbon alkylene group; the M^+ ion is selected from the class consisting of a metal cation, a substituted ammonium cation, an ammonium cation, a substituted hydrazinium cation, and a hydrazinium cation; and the X anion is an ion selected from the class consisting of fluoride, chloride, alkoxide, carboxylate, hydroxyl, and carbonate ions. The reaction, when a salt is reacted with the dinitramine, is shown in the following equation:

$$L_4ZR'N(NO_2)_2 + MX \text{ -------> } MN(NO_2)_2 + L_4ZX + R$$

An example of such a dinitramine precursor is 2-trimethylsilylethyl-N,N-dinitramine having the formula $(CH_3)_3Si(CH_2)_2-N(NO_2)_2$.

The dinitroamine precursor may be formed by known prior art methods such as described in Hamel et al. U.S. Patent 3,428,667, cross-reference to which is hereby made; or as described in the aforementioned Third Quarterly Report of AF Contract 04(611)-8549, cross-reference to which is also made.

Alternatively, in accordance with one aspect of the invention, the dinitramine precursor may be formed directly from an aliphatic isocyanate using stoichiometric quantities of nitronium tetrafluoroborate

and nitric acid in acetonitrile as the nitrating system as shown in the equation below:

$$R\text{-}N{=}C{=}O \xrightarrow[NO_2^+BF_4^-,\ CH_3CN]{HNO_3} R\text{-}N(NO_2)_2$$

The degradation reaction of the $RN(NO_2)_2$ dinitramine with the MX salt takes places in an inorganic or organic solvent which preferably will be a polar solvent, such as water, alcohols, or acetone, at any pH compatible with the starting materials, but usually within a range of from about 3 to about 10.

The temperature of the degradation reaction may range from -40°C to 150°C, preferably from about 0°C to about 20°C. The degradation reaction may be carried out at ambient pressure for a time period which may range from as short as 1 minute to as long as one week, depending upon the reactivity of the starting materials, the temperature selected, and the desired yield. Usually the reaction will be carried out for a period of from about 1 to about 2 hours.

b. Second Method of Preparing Dinitramide Salts

The dinitramide salts of the invention may also be prepared by the initial reaction of nitramide (having the formula NH_2NO_2) with a nitrating agent such as nitronium tetrafluoroborate having the

formula NO_2BF_4 to form the free acid $HN(NO_2)_2$ as shown in the following equation:

$$NH_2NO_2 + NO_2BF_4 \text{ -------> } HN(NO_2)_2 + HBF_4$$

Other nitrating agents which may be reacted with nitramine instead of nitronium tetrafluoroborate include $(NO_2^+)_2(S_2O_7^{-2})$, $NO_2^+ AlCl_4^-$, N_2O_5, NO_2F, $NO_2^+ PF_6^-$, $NO_2^+ AsF_6^-$, $NO_2^+ SbF_6^-$, acetylnitrate, trifluoroacetylnitrate, trifluoroacetylnitrate in combination with catalytic BF_3, acetonecyanohydrin nitrate in combination with catalytic BF_3, and any one of these in combination with nitric acid.

This intermediate product is then reacted with the previously described metal-containing compound or nitrogen-containing compound, such as ammonia, hydrazine, and the previously described MX salt to form the dinitramide salt of the invention, which, in the case of the MX salt, is illustrated in the following equation:

$$HN(NO_2)_2 + MX \text{ -------> } MN(NO_2)_2 + HX$$

If hydrazine is used as the neutralizing agent, extreme care should be exercised when handling the resultant product due to its possible shock sensitivity.

It should be noted that the above reaction works well in the absence of NO^+, NO, and NO_2, i.e. when less than about 5 wt.% total of any or all of the above oxides of nitrogen are present. Therefore, in

accordance with a preferred embodiment of the invention, the reagents used in this reaction should be made or purified to provide a content of NO^+, NO, and/or NO_2 less than about 5 wt.%.

The following examples will serve to further illustrate the invention.

Example I

To form a 2-(trimethylsilylethyl)-N,N-dinitramine precursor, an ice-cooled mixture of 1.45 grams (11 millimoles) of nitronium tetrafluoroborate, 10 ml of acetonitrile, and 700 milligrams (11 millimoles) of 99+% HNO_3 (under argon) was formed, and then 10 millimoles of 2-(trimethylsilylethyl)isocyanate was added, avoiding fume-off by controlling the rate of addition as appropriate. The reaction was stirred for 15 minutes at 0°C, diluted to 25 ml with $CHCl_3$, and filtered rapidly through a 1" x 3" plug of SiO_2, eluting with 100 ml of $CHCl_3$. Chromatography of the crude product, eluting $CHCl_3$ over SiO_2 and collecting the fastest-moving, UV active material (R_f=0.5), resulted in collection of 500 milligrams of the desired 2-(trimethylsilylethyl)-N,N-dinitramine precursor, about a 25% yield.

A 1-adamantyl-N,N-dinitramine compound was formed from 1-adamantylisocyanate; and a 1,6-bis(N,N-dinitramino)hexane compound was formed from 1,6-hexane isocyanate using the same procedure as described above.

Example II

To about 2.5 milliliters of 2-(trimethylsilylethyl)-N,N-dinitramine, such as formed in Example I, dissolved in 20 ml of acetonitrile and maintained at 20°C was added 1 gram of tetramethylammonium fluoride. The solution was stirred for about 120 minutes. The tetramethylammonium N,N-dinitramide salt product was then recovered by crystallization from ethyl acetate. The product yield was 900 milligrams or about a 50% yield.

The same procedure was repeated by reacting tetrabutylammonium fluoride and cesium fluoride respectively with 2-(trimethylsilylethyl)-N,N-dinitramine to form the corresponding tetrabutyl ammonium dinitramide and cesium dinitramide salts.

Example III

2 millimoles of nitramide was dissolved in 4 ml of anhydrous acetonitrile cooled under argon to a temperature of -10°C, and then treated with 300 mg (2.3 millimoles) of nitronium tetrafluoroborate. The reaction mixture was stirred for 10 minutes and was then added to a stirred mixture of 8 ml of 1 molar NH_3/2-propanol in 100 ml of ethyl ether. The mixture was stirred for 5 minutes. The mixture was evaporated to dryness, triturated with 10 ml of 1:1 acetone/ethyl acetate, filtered, evaporated to dryness, and 0.15 grams of ammonium dinitramide was crystallized from 2 ml of butanol.

Example IV

2 millimoles of nitramide was dissolved in 4 ml of anhydrous acetonitrile cooled under argon to a temperature of -10°C, and then treated with 300 mg (2.3 millimoles) of nitronium tetrafluoroborate. The reaction mixture was stirred for 10 minutes and was then added to 8 ml of 1 molar aqueous potassium carbonate. The mixture was stirred for 5 minutes. The mixture was evaporated to dryness, triturated with 10 ml of 1:1 acetone/ethyl acetate, filtered, evaporated to dryness, and 0.15 grams of potassium dinitramide was crystallized from 2 ml of butanol.

Example V

To show the stability and utility of the dinitramide salts of the invention, Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) tests were carried out to determine the thermal stability of the compounds as well as the energy derived from each compound. Acid and base stability tests were also carried out to determine the pH range at which the compounds were stable. The results are shown in the following table:

Table I

Dinitramide Salt	Cs^+ $^-N(NO_2)_2$	NH_4^+ $^-N(NO_2)_2$	$N_2H_5^+$ $^-N(NO_2)_2$
Onset of Decomposition	190°C	140°C	150°C
pH Stability	0-14	0-14*	0-10
Melting Point	83°C	92°C	83°C
Energy of Decomposition	62.4 KJ/Mole	270 KJ/Mole	258 KJ/Mole

* loss of NH_3 above 10

Thus, the invention provides novel dinitramide salts useful as oxidizers in rocket fuels and which exhibit high temperature stability, high energy density, and an absence of smoke generating halogens. The dinitramide salts of the invention are meltable and pumpable oxidizers which may be used in start-stop rocket engines instead of other less stable oxidizers.

Having thus described the invention what is claimed is:

1. A N,N-dinitramide salt having the formula $MN(NO_2)_2$ where M is a cation selected from the class consisting of a metal ion and a nitrogen-containing ion.

2. The N,N-dinitramide salt of claim 1 wherein M is a mono, di, or trivalent metal cation selected from the class consisting of Li, Na, K, Rb, Cs, Ca, Ba, Sr, Mg, Cu, Ag, Au, Zn, Cd, Hg, Al, Sc, Y, Ga, In, Lanthanide elements (57-71), Ti, Zr, Hf, Ge, Sn, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, and Pt.

3. The N,N-dinitramide salt of claim 2 wherein M is a metal cation selected from the class consisting of Li, Na, K, Be, and Mg.

4. The N,N-dinitramide salt of claim 1 wherein M is a 1-8 nitrogen-containing cation.

5. The N,N-dinitramide salt of claim 1 wherein M is a 1-8 nitrogen-containing cation having the formula $R_nH_mN_z^{+z}$, wherein n = 1 to 8, k = 0 to 2+n, z = 1 to n, m = n+2+z-k, and each R is the same or different 1-6 carbon straight chain or branched alkyl.

6. The N,N-dinitramide salt of claim 1 wherein M is a nitrogen-containing cation selected from the class consisting of guanidinium; triaminoguanidinium; nitronium; nitrosonium; a 1-10,000 nitrogen polymer of ethyleneimine; cubane-1,4-bis ammonium ion; cubane-1,2,4,7-tetra ammonium ion; cubane-1,2,3,4-tetra ammonium ion; cubane-1,3,5,7-tetra ammonium ion; cubane-1,2,3,4,7-penta ammonium ion; and cubane-1,2,4,6,8-penta ammonium ion.

7. The N,N-dinitramide salt of claim 1 wherein said salt is the reaction product of a nitramine compound with a compound selected from the class consisting of ammonia, hydrazine, and a salt having the formula MX wherein X is an ion selected from the class consisting of fluoride, chloride, hydroxyl, carbonate, alkoxide, and carboxylate.

8. The N,N-dinitramide salt of claim 7 wherein said salt is the reaction product of a dinitramine having the formula $L_nZR'N(NO_2)_2$ with said MX compound, wherein n is 1 to 3; L is the same or different 1-6 carbon alkyl, aryl, hydrogen, halogen, amine, or ether group; Z is an element selected from the class consisting of Si, Sn, Ge, As, B, Sb, Bi, Pb, and Hg; and R' is a 1 to 6 carbon alkylene group; the M^+ ion is selected from the class consisting of a metal cation, a substituted ammonium cation, an ammonium cation, a substituted hydrazinium cation, and a hydrazinium cation; and the X anion is a halogen ion selected from the class consisting of fluoride and chloride ions.

9. The N,N-dinitramide salt of claim 7 wherein said dinitramide salt is the reaction product of a nitramine compound having the formula NH_2NO_2 with a nitrating agent selected from the class consisting of nitronium tetrafluoroborate, $(NO_2^+)_2(S_2O_7^{-2})$, NO_2^+ $AlCl_4^-$, N_2O_5, NO_2F, NO_2^+ PF_6^-, NO_2^+ AsF_6^-, NO_2^+ SbF_6^-, acetylnitrate, trifluoroacetylnitrate, trifluoroacetylnitrate in combination with catalytic BF_3, acetonecyanohydrin nitrate in combination with catalytic BF_3, and any one of these in combination with nitric acid, and to form an acid having the formula $HN(NO_2)_2$ which is then reacted with a compound selected from the class consisting of a metal-containing compound and a nitrogen-containing compound to form said dinitramide salt having the formula $MN(NO_2)_2$.

10. The N,N-dinitramide salt of claim 1 wherein said salt is the reaction product of a nitramine compound having the formula NH_2NO_2 with nitronium tetrafluoroborate to form an acid having the formula $HN(NO_2)_2$, which is then reacted with a compound selected from the class consisting of a metal-containing compound and a nitrogen-containing compound to form said dinitramide salt having the formula $MN(NO_2)_2$.

11. A N,N-dinitramide salt having the formula $MN(NO_2)_2$ where M is a cation selected from the class consisting of:

a) mono, di, and trivalent metal ions elected from the class consisting of Li, Na, K, Rb, Cs, Ca, Ba, Sr, Mg, Cu, Ag, and Au, Zn, Cd, Hg, Al, Sc, Y, Ga, In, Lanthanide elements (57-71), Ti, Zr, Hf, Ge, Sn, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, and Pt;

b) a 1-8 nitrogen-containing cation having the formula $R_nH_mN_z^{+z}$, wherein n = 1 to 8, k = 0 to 2+n, z = 1 to n, m = n+2+z-k, and each R is the same or different 1-6 carbon straight chain or branched alkyl; and

c) a nitrogen-containing cation selected from the class consisting of guanidinium; triamino-guanidinium; nitronium; nitrosonium; a 1-10,000 nitrogen polymer of ethyleneimine; cubane-1,4-bis ammonium ion; cubane-1,2,4,7-tetra ammonium ion; cubane-1,2,3,4-tetra ammonium ion; cubane-1,3,5,7-tetra ammonium ion; cubane-1,2,3,4,7-penta ammonium ion; and cubane-1,2,4,6,8-penta ammonium ion.

12. A method of making a N,N-dinitramide salt having the formula $MN(NO_2)_2$ wherein M is a cation selected from the class consisting of a metal cation and a nitrogen-containing cation which comprises reacting a dinitramine compound with a compound selected from the class consisting of a metal-containing compound and a nitrogen-containing compound.

13. A method of making a N,N-dinitramide salt having the formula $MN(NO_2)_2$ wherein M is a cation selected from the class consisting of a metal cation and a nitrogen-containing cation which comprises reacting a dinitramine compound with a compound selected from the class consisting of ammonia, hydrazine, and a salt having the formula MX wherein X is a halogen anion selected from the class consisting of fluoride and chloride.

14. The method of claim 13 which includes reacting a dinitramine having the formula $L_nZR'N_c(NO_2)_2$ with said ammonia, hydrazine, or MX salt wherein n is 1 to 3; L is the same or different 1-6 carbon alkyl, aryl, hydrogen, halogen, amine, or ether group; Z is an element selected from the class consisting of Si, Sn, Ge, As, B, Sb, Bi, Pb, and Hg; R' is a 1 to 6 carbon alkylene group; the M^+ ion is selected from the class consisting of a metal cation, a substituted ammonium cation, an ammonium cation, a substituted hydrazinium cation, and a hydrazinium cation; and the X^- anion is an ion selected from the class consisting of fluoride, hydroxyl, carbonate, alkoxide, carboxyl, and chloride ions.

15. The method of claim 14 wherein said dinitramine having the formula $RN(NO_2)_2$ is formed from an aliphatic isocyanate having the formula R-N=C=O using stoichiometric amounts of nitronium tetrafluoroborate and nitric acid in acetonitrile.

16. A method of making a N,N-dinitramide salt having the formula $MN(NO_2)_2$ wherein M is a cation selected from the class consisting of a metal cation and a nitrogen-containing cation which comprises:

a) reacting nitramide having the formula NH_2NO_2 with a nitrating agent to form an acid having the formula $HN(NO_2)_2$; and

b) reacting said acid with a compound selected from the class consisting of ammonia, hydrazine, and a salt having the formula MX wherein X is a halogen anion selected from the class consisting of fluoride, hydroxyl, carbonate, alkoxide, carboxyl, and chloride ions.

17. The method of claim 16 wherein said step of reacting nitramide with said nitrating agent further comprises reacting said nitramide with a nitrating agent selected from the class consisting of nitronium tetrafluoroborate, $(NO_2^+)_2(S_2O_7^{-2})$, NO_2^+ $AlCl_4^-$, N_2O_5, NO_2F, NO_2^+ PF_6^-, NO_2^+ AsF_6^-, NO_2^+ SbF_6^-, acetylnitrate, trifluoroacetylnitrate, trifluoroacetylnitrate in combination with catalytic BF_3, acetonecyanohydrin nitrate in combination with catalytic BF_3, and any one of these in combination with nitric acid, to form said acid having the formula $HN(NO_2)_2$.

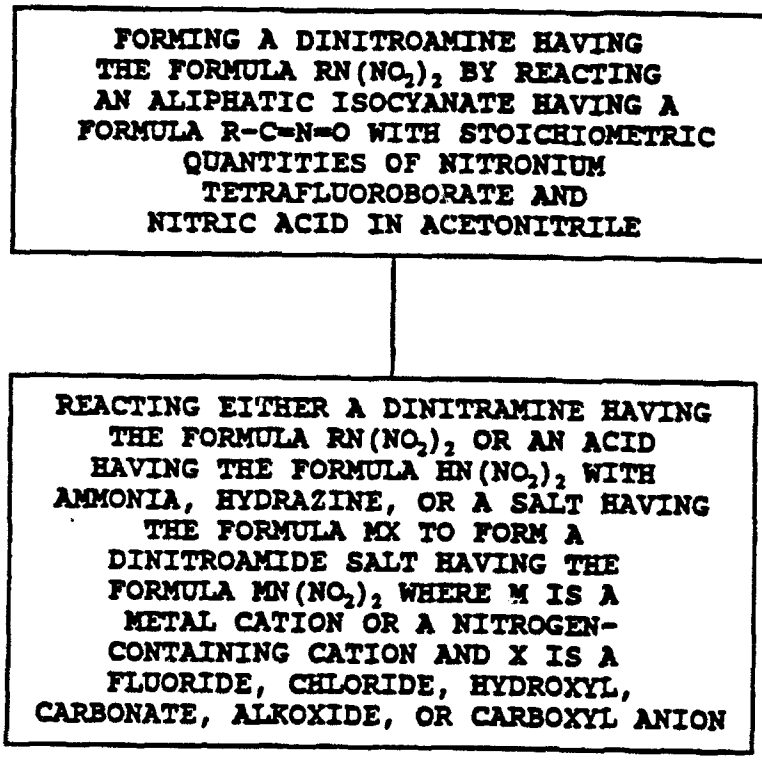
18. The method of making a N,N-dinitramide salt of claim 16 which comprises:

a) reacting nitramide having the formula NH_2NO_2 with nitronium tetrafluoroborate to form an acid having formula $HN(NO_2)_2$; and

b) reacting said acid with said salt having the formula MX.

19. The method of claim 16 wherein said step of reacting said acid with a compound selected from the class consisting of ammonia, hydrazine, and a salt having the formula MX is carried out at a temperature of from about -40°C to about 150°C at ambient pressure for a time period ranging from about 1 minute to about 168 hours.

20. The method of claim 16 wherein said step of reacting said acid with a compound selected from the class consisting of ammonia, hydrazine, and a salt having the formula MX is carried out at a temperature of from about 0°C to about 20°C at ambient pressure for a time period ranging from about 1 hour to about 2 hours.


FORMING A DINITROAMINE HAVING THE FORMULA $RN(NO_2)_2$ BY REACTING AN ALIPHATIC ISOCYANATE HAVING A FORMULA R-C=N=O WITH STOICHIOMETRIC QUANTITIES OF NITRONIUM TETRAFLUOROBORATE AND NITRIC ACID IN ACETONITRILE
REACTING EITHER A DINITRAMINE HAVING THE FORMULA $RN(NO_2)_2$ OR AN ACID HAVING THE FORMULA $HN(NO_2)_2$ WITH AMMONIA, HYDRAZINE, OR A SALT HAVING THE FORMULA MX TO FORM A DINITROAMIDE SALT HAVING THE FORMULA $MN(NO_2)_2$ WHERE M IS A METAL CATION OR A NITROGEN-CONTAINING CATION AND X IS A FLUORIDE, CHLORIDE, HYDROXYL, CARBONATE, ALKOXIDE, OR CARBOXYL ANION

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SIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)[6]

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t.Cl. 5	C01B ; C06B

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

DCUMENTS CONSIDERED TO BE RELEVANT[9]

y *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No.[13]
	GB,A,1 126 591 (AEROJET-GENERAL CORP.) December 5, 1968 see the whole document see page 1, line 44 - line 63 & US,A,3 428 667 (HAMEL ET AL.) February 18, 1969 cited in the application	1,4 7,9,10, 12,13, 16-20
	EP,A,324 609 (MORTON THIOKOL) July 19, 1989 cited in the application see the whole document	6,11

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		JP-A- 2000741	05-01-90

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Appendix C

A NEW SYNTHESIS OF ALKYL-N,N-DINITRAMINES BY DIRECT NITRATION OF ISOCYANATES

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SYNTHETIC COMMUNICATIONS, 21(7), 945-949 (1991)

A NEW SYNTHESIS OF ALKYL-N,N-DINITRAMINES BY DIRECT NITRATION OF ISOCYANATES

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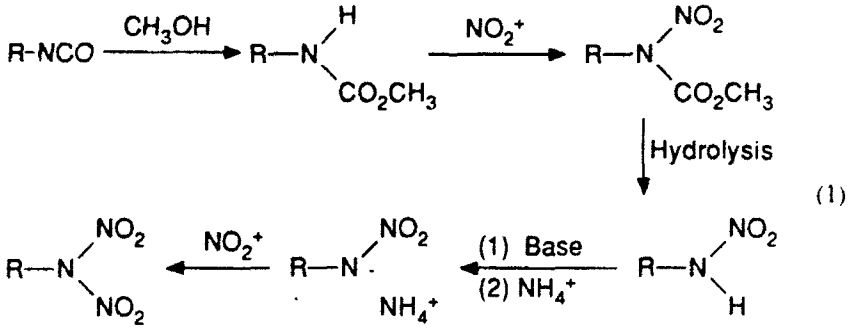
ABSTRACT

A facile conversion of aliphatic isocyanates to N,N-dinitramines has been developed. An aliphatic isocyanate is treated with a mixture of nitronium fluoroborate and nitric acid in acetonitrile giving fair yields and simplifing the existing synthesis.

The N,N-dinitramine function is a highly labile functional group accessible only by difficult preparative procedures. Recently, renewed interest has developed in preparing N,N-dinitramines as possible energetic groups for propellant applications. The established method,[1] takes four steps and involves the preparation of an alkyl nitramine via the N-nitromethylcarbamate followed by nitration with nitronium ion, according to Equation 1.



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* To whom correspondence should be addressed

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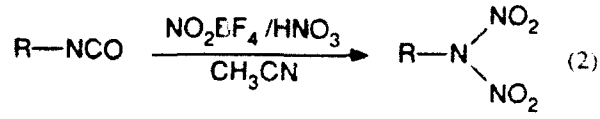
We report here a new, simple, one-step synthesis of N,N-dinitramines from aliphatic isocyanates, using stoichiometric quantities of nitronium tetrafluoroborate and nitric acid in acetonitrile as the nitrating system, according to Equation 2.

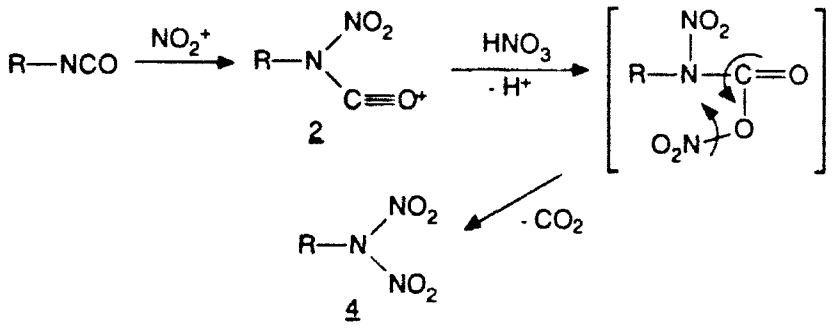


(2)

This route differs from the previous work in that it is only one step instead of four, and requires the presence of both nitric acid and high quality nitronium tetrafluoroborate in the reaction medium. If either reagent is absent, no N,N-dinitramine is formed.

We propose the simple mechanism shown in Scheme I, in accordance with the observation of Ledebev et al (Scheme I) who reacted isocyanates with nitronium ions in the absence of nitric acid to give monoalkyl-mononitramino compound via intermediate 2.[2] Adding an aliphatic isocyanate to a preformed, ice-cooled mixture of acetonitrile, nitric acid, and nitronium tetrafluoroborate results in the initial formation of the corresponding acylium ion 2 to which HNO_3 is added, then losing a proton and CO_2, to give the corresponding aliphatic N,N-dinitramine 4. Consistent with this mechanism is our observation that no N,N-dinitramines are formed when the reaction is run in the absence of free nitric acid which presumably acts as a nucleophile toward acylium ion 2. An alternative to the proposed mechanism below is the direct addition of N_2O_5 (formed by the reaction of NO_2BF_4 with HNO_3) across the alkyl isocyanate giving the same reactive intermediate shown below also giving 4.

This reaction is most successful with primary alkyl isocyanates. When 1-adamantyl isocyanate was subjected to the conditions of this procedure, only a trace (<1%) of the desired N,N-dinitramine was formed, with the remainder of the substrate transformed into a complex mixture. This result indicates a high sensitivity either to steric hindrance or to the stability of the ternary carbonium ion or radical formed if the dinitramine group leaves and then rearranges. We would expect that the dinitramide groups is an excellent leaving group and obviously quite



Scheme 1: Proposed Mechanism for N,N-Dinitramine Synthesis

Table I

Substrate	Product	Yield
n-Butyl isocyanate	1-(N,N-Dinitramino) butane	35%
Methyl isocyanate	N,N-Dinitramino-methane	30%
1-Adamantyl isocyanate	1-(N,N-Dinitramino) adamantane	<1%
Hexamethylene diisocyanate	1,6-bis(N,N-Dinitramino)hexane	10%
Ethane-1,2-diisocyanate	1,2-bis(N,N-Dinitramino)ethane	-0-
2-(Trimethylsilyl-ethyl)-1-isocyanate	1-(N,N-Dinitramino)-2-trimethylsilyl-ethane	25

labile when attached to a ternary position such as the 1-position of adamantane. Hexamethylene diisocyanate is converted in 10% yield, the square of the yield obtained for monofunctional substrates, indicating that the two distant functional groups are not interacting in this case.

The substrates investigated are shown in Table I, along with the yields. The overall yields from this route are no better than those of previous syntheses, but the transformation is accomplished in one rather than four steps.

EXPERIMENTAL

CAUTION: All the products described in this paper are potentially explosive and should be handled in 0.5-g quantities and stored at 0°C. All NMR spectra were obtained on a Varian EM-360 spectrometer. IR spectra were obtained on a Perkin-Elmer 1420 Infrared spectrophotometer. Elemental analysis could not be obtained because of the marked instability of the products. All thin-layer chromatography was run by elution of $CHCl_3$ over silica gel.

General Procedure for Conversion of Isocyanates to N,N-Dinitramines. To an ice-cooled mixture of 1.45 g (11 mmol) of nitronium tetrafluoroborate, 10 mL of acetonitrile, and 700 mg (11 mmol) of 99+% HNO_3 (under argon) was added 10 mmol of aliphatic isocyanate, avoiding fume-off by controlling the rate of addition as appropriate. The reaction mixture was then stirred for 15 min at 0°C, diluted to 25 mL with $CHCl_3$, filtered rapidly through a 1 x 3-in. plug of SiO_2, and eluted with 100 mL of $CHCl_3$. Chromatography of the crude product, elution $CHCl_3$ over SiO_2, and collection of the fastest moving UV-active material ($R_f = 0.5$) yielded the desired dinitramines in fair quantity. N,N-Dinitro-1-butylamine and N,N-dinitromethylamine show spectral properties identical to those of known samples synthesized by established methods.[1]

1-Adamantyl-N,N-dinitramine: IR (Neat) 2900, 1610 (s), 1270 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2-2.5 (m) TLC: $R_f = 0.7$ ($CHCl_3/SiO_2$) bleaches I_2.

1,6-bis(N,N-dinitramino)hexane: IR (Neat 2940, 2860, 1640 (s), 1600 (s), 1340 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.1 (t, 4H, J = 6 Hz, CH_2-N) δ 1.2-1.9 (m, 6H, CH_2) TLC: $R_f = 0.5$ ($CHCl_3/SiO_2$) bleaches I_2.

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